WRDC-TR-89-4069

ELECTRO-DEPOSITED PRIMER DEVELOPMENT AND LOW-POLLUTING PRIMER EVALUATION

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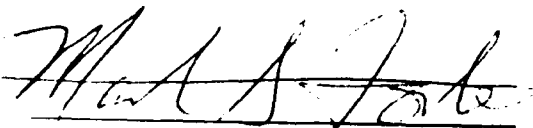Wright Patterson Air Force Base, Ohio   45433-6533
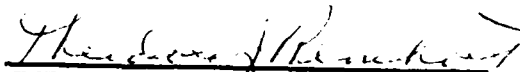
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19 ABSTRACT (Continue on reverse if necessary and identify by block number)

The objectives of this Air Force program are to develop, evaluate, demonstrate, and qualify an electro-deposited (ED) corrosion resistant primer system for metal bonding suitable for use with 350°F curing adhesives and to evaluate other low-polluting primer systems (such as water-base spray and dip systems or inorganic primers) which would be suitable for use with 350°F curing adhesives.

Several electro-deposited primer formulations were evaluated to determine the optimum primer. The best primer developed met all of the initial adhesive bonded corrosion performance criteria in the laboratory. Scale-up to 6-gallon, 20-gallon, and eventually 200-gallon demonstration of the electro-deposited priming process was planned; however, the primer was not successfully demonstrated. Additional work on the primer formulation and/or process equipment design is necessary and could not be accomplished within the provisions of this contract. Water-base primers were tested; the most promising was further tested and readily exceeded program requirements.

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SUMMARY

This is the final report (CDRL #5) on Contract Number F-33615-86-C-5009, "Electro-Deposited Primer Development and Low-Polluting Primer Evaluation" for the period of September 8, 1986 through November 16, 1988.

An electrodeposited primer is viewed as a good approach for satisfying environmental issues and improving corrosion resistance of adhesive bonded structures. Improved corrosion resistance is forecast as the likely result of coating all exposed surfaces through electrochemical priming action. Additional benefits forecast are the reduction of primer loss typical of current spray application methods, and improvement of manufacturing output by priming the entire surfaces of many details in less than 1 minute of processing time.

The 3M Company previously developed electrodeposited primers showing adhesive bond strength performance capability to 325°F/350°F, which is a specific goal for the program. In Phase I of the program the 3M Company, as a subcontractor to Rohr, optimized electrodeposited primer formulations and selected the best for a scale-up study to verify it as a production viable primer for use on F-111 aircraft repair. The primer developed met all of the initial adhesive-bond and corrosion-performance criteria when applied to specimens under laboratory conditions.

A second requirement of the Phase I work task was to scale up the optimized formulation in production prototype equipment. The equipment selected was based upon electrodeposited primer facility design made by Lockheed in AFWAL-TR-87-4085. Rohr's first scale-up in the program was to screen the electrodeposited primer optimized for this program by trial in a 6-gallon electrodeposition facility. Standard military specification qualification tests for adhesive performance were used to evaluate the primer. The program was to later address two further stages of scale-up in Phase II, 20 gallons and 200 gallons, leading to completion of a full complement of qualification tests to MMM-A-132 and MIL-A-25463.

Problems were encountered controlling primer thickness on specimens coated in the 6-gallon production prototype electrodeposition tank to the values established as optimum in the laboratory. Perhaps as a result of this difficulty, we were unable to meet several of the military specification qualification values required by the program. We also discovered a porous condition in the primer film, especially in the thin coatings required to meet bond strength criteria.

Rohr modified the 6-gallon electrodeposition tank facility extensively, and several batches of electrodeposited primer were used during the various improvement efforts without success. We concluded at this point that additional laboratory work on optimizing primer formulation and/or investigating alternative tank designs was required to make the primer functional in a production environment.

In addition to the electrodeposited primer optimization effort, a search of industry, including literature, for water-base primer materials was conducted and candidate primers were tested. This effort was limited to a maximum of 25 percent of the contract funds. Water-base primers were generally considered less desirable than electrodeposited primers because they require more application labor, do not provide inherent coverage of all surfaces, and produce undesirable overspray.

Water-base primer systems are being considered by industry as a replacement to organic solvent-base primer systems in current adhesive bonding systems because organic solvents pose environmental impact problems and must be reduced/eliminated or be dealt with using costly recovery/incineration systems.

Rohr identified three water-base primers applied by conventional spray application techniques which demonstrated a capability for meeting military specification qualification requirements. We selected the best primer from the three candidates on the basis of performance and ease of application. The primer was tested to the same test matrix used to screen the electrodeposited primer. The primer readily exceeded program requirements for these tests. We concluded that the primer was a potential candidate for full qualification testing but that its corrosion resistance was marginal.

The program did not provide for any reworking of the water-base spray formulation or for spray application process development. We believe that all of the water-base primers could benefit from these actions.

The program was terminated when it became apparent that the electro-deposited primer formulation could not be successfully scaled up within the provisions of the contract.

FOREWORD

This program, Electrodeposited Primer Development and Low-Polluting Primer Evaluation, was conducted by Rohr Industries, Inc., under Contract F33615-86-C-5009. The program was performed under the technical direction of Mr. Mark Forte, Project Engineer - WRDC, Materials Laboratory, Wright-Patterson Air Force Base, Ohio.

This final report presents the results of work accomplished during the period of September 8, 1986 through November 16, 1988. The overall program was performed under the direction of Rohr Industries' R.H. Greer, Program Manager, and Dr. J. Patel, Principal Investigator. The 3M Company was under contract to Rohr Industries to perform Phase I, Task I Cathodic Electrophoretically Deposited Structural Adhesive Bonding Primer (CEDSABP) development, to supply CEDSABP material, and to perform analytical services for the program. The 3M effort was under the direction of Dr. A. Pocius, Program Manager, and T. Wilson, Principal Investigator.

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1/ INTRODUCTION

The objective of this Air Force program is to develop, evaluate, demonstrate, and qualify an electrodeposited (ED) corrosion resistant primer system for metal bonding suitable for use with 350°F curing adhesives.

A second objective of the program is to evaluate other low-polluting primer systems (such as water-base spray and dip systems or inorganic primers) which will be suitable for use with 350°F curing adhesives.

The objectives of the program are motivated by a desire to eliminate environmentally objectionable solvents currently found in adhesive primer materials. Federal and state environmental regulations limit the amounts of solvents and may hinder the Air Force's capability for repairing high-performance aircraft where solvent-base adhesive primer materials are currently used. Other problems inherent in the use of spray-applied primers are nonuniform corrosion protection, poor control of primer thickness, and variable strength of the adhesive bond. The electropriming process will eliminate primer waste due to overspray and is adaptable to automation which should result in reduced costs.

The program is composed of two phases, each of which comprise several tasks. In Phase I an electrodeposited primer material is to be optimized for 325°F service temperature use and other service requirements for military aircraft. Primer compatibility with 350°F curing adhesive bonds

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to aluminum and titanium substrates are also studied. This task is performed by the 3M Company under subcontract to Rohr Industries.

Also in Phase I, Rohr canvasses the literature and industry sources for water-base primer materials having potential for meeting the performance objectives of the program. Water-base primer materials which show promise are screened in a test program which examine primer application methods and adhesive bond strength performance.

Phase I concludes with an extensive screening program (Task III) which assesses the ability of the ED primer developed and optimized in Task I by 3M to meet the objectives of the program. This test program consists of performing the conventional military and federal tests for adhesive bond performance on bonded aluminum adherends, aluminum adherend/ honeycomb sandwich, and titanium adherend test configurations. The best performing water-base primer is compared with the ED primer in the screening program using two different adhesive systems. Special attention is given to the failure modes occurring through instrumental surface analysis examinations.

Phase II involves the scale-up of electrodepositable primer manufacture and demonstration of the ED priming process through a 200-gallon production tank installation. Due to difficulties encountered during Task III screening in Phase I, it becomes apparent that additional work on the primer formulation and/or process equipment design is necessary. This work cannot be accomplished within the provisions of the contract; the contract has been terminated at the request of the Air Force.

2/ PHASE I, TASK I
ELECTRODEPOSITED PRIMER OPTIMIZATION

2.1   INTRODUCTION

Current aircraft are primed with corrosion inhibiting primers that are
generally organic solvent thinned, epoxy and phenolic based. These
primers are cured at 250°F to 350°F and contain an organic insoluble,
slightly water soluble corrosion inhibiting pigment (usually a chromate
salt). The performance characteristics that a structural adhesive
bonding primer must have are listed in Table 2-1. Current materials have
the necessary characteristics, but suffer several drawbacks:

- They are organic solvent thinned and do not comply with new,
  stricter pollution control regulations.

- They are applied by "line-of-sight methods" and cannot be
  used to coat inaccessible portions of complex parts (e.g.,
  the interior of a honeycomb cell).

- They are relatively brittle (in comparison to the adhesive)
  and if the primer application is too thick, bond performance
  can be reduced (see Section 6, Item 1).

Table 2-1. Performance Characteristics of Structural
Adhesive Bonding Primer

1. Provides protection against corrosion inside and outside of the
    bonded joint

2. Provides a surface to which the adhesive can easily bond

3. Provides protection for the surface-prepared adherends
    before bonding

4. Exhibits resistance to aircraft fluids such as jet fuel,
    hydraulic fluids, solvents, etc.

5. Is capable of transferring structural load from the adherend
    through the surface preparation to the adhesive

6. At appropriate thickness, displays no deleterious effects on
    the shear or peel properties of the adhesive bond

2.1.1 **ELECTRODEPOSITABLE COATINGS** -- Electrodepositable coatings are widely used in the automobile and appliance manufacturing industries. This coating technology has the following advantages:

- It is self-leveling.

- It has the ability to coat surfaces that are inaccessible by "line-of-sight" methods.

- It is self-limiting in thickness.

The above capabilities are attributable to the fact that the coating application process is electrochemical in nature. The technology is further described in Section 2.1.3. The features of electrodepositable coatings, described above, are not found in other "state-of-the-art" primers. However, current electrodepositable coatings cannot, in general, conform to the requirements of a structural adhesive bonding primer that are listed in Table 2-1.

The special experience gained in the development of a coating can be used in the development of a structural adhesive binding primer; however, additional knowledge in the formulation of structural adhesive bonding systems is necessary because of the strength requirements and other characteristics listed in Table 2-1. 3M has invested the expertise gained during 30 years of formulation work in structural adhesives and bonding primers into this program.

2.1.2 **CATHODIC ELECTROPHORETICALLY DEPOSITED STRUCTURAL ADHESIVE BONDING PRIMERS (CEDSABPs)**

2.1.2.1 **Previous Air Force Funded Contract Work** -- Attempts have been made to develop electrophoretically depositable structural adhesive bonding primers. The first efforts were carried out under Air Force Contracts F33615-78-C-5050 and F33615-C-5301 and described in several reports. (See Section 6, Items 2, 3, and 4.) The CEDSABPs developed in

these contracts apparently meet the requirements of a 180°F service structural adhesive bonding primer.

2.1.3 BACKGROUND ON ELECTRODEPOSITABLE PAINTS -- Electrodepositable paints have been used in industry for approximately 25 years. The early technology in these paints was based on water soluble polymers bearing a negative charge. The negatively charged water soluble polymer is placed in an electrochemical cell, and the electrodes in the cell are appropriately biased. The negatively charged polymer migrates to the anode by a phenomenon known as electrophoresis. The appropriate technological term for this paint is an "anodic electrophoretically depositable paint." Electrode reactions at the anode generate protons which discharge the negatively charged water soluble polymer. This results in an uncharged and water insoluble substance deposited on the anode surface. The area on the anode on which the polymer has deposited becomes insulated against the passage of current. In the absence of current, the polymer cannot deposit in that insulated area, and polymer deposition moves to another area on the anode on which the polymer is deposited.

Unfortunately, the improvement in corrosion protection afforded by anodic electrodeposited paint was limited because the anode, under the applied potential, generates metal ions that become part of the deposited film. These metal ions stain the film and also reduce corrosion protection.

The other electrode in the electrochemical cell is negatively charged and is known as the cathode. The electrode reaction which takes place in water at the cathode generates hydroxide ions rather than metal ions. (See Figure 2-1.) A paint having a polymer that is positively charged would electrophoretically migrate to the cathode in a fashion that is analogous to the process for anodic paints. However, the positive features of an electrophoretically depositable paint are obtained without the negative features of anodic deposition. The improvements in appearance and corrosion protection obtained by cathodic deposition are so significant that virtually all automobile chassis and appliance parts are now initially painted with cathodic electrophoretically depositable paints.
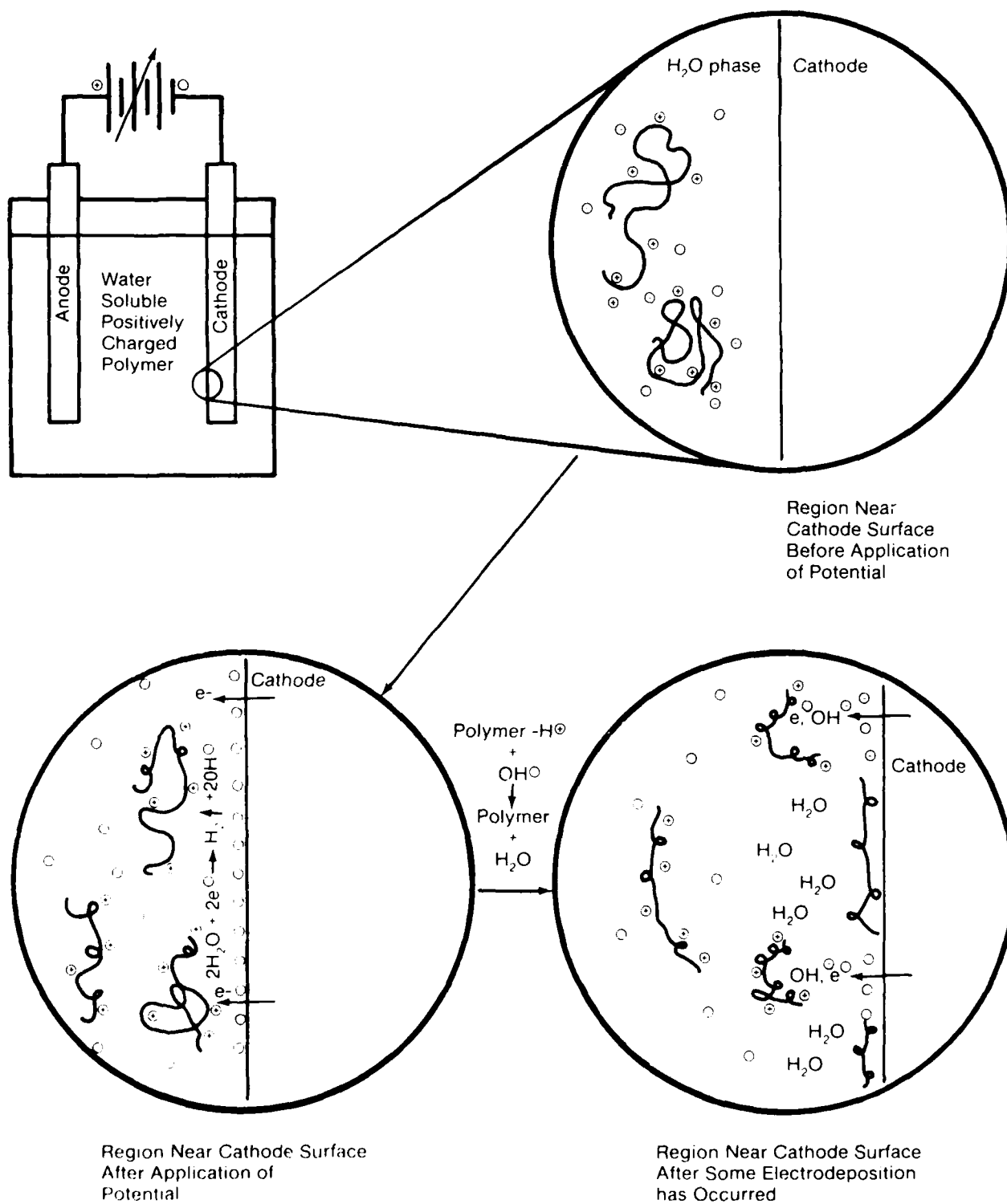
Figure 2-1. Schematic of the Cathodic Electrodeposition Process

2.1.4   BACKGROUND ON STRUCTURAL ADHESIVE BONDING PRIMERS --
Structural adhesive bonding is a well-known method for manufacturing lightweight honeycomb sandwich aircraft structures. The durability of adhesive bonded structures is strongly dependent on factors which include the following:

*   Proper surface preparation of the adherend

*   Use of a corrosion inhibiting primer

*   Use of a corrosion inhibited honeycomb core.

Current aircraft adherends are primed with corrosion inhibiting primers that are generally organic solvent thinned, epoxy and/or phenolic based. They are cured at 250° to 350°F and contain an organic insoluble, slightly water-soluble corrosion inhibiting pigment (usually a chromate salt). These primers are applied by standard spray methods. The performance characteristics and drawbacks of these solvent-thinned primers are discussed in Paragraph 2.1.

2.1.5   THE RELATIONSHIP BETWEEN STRUCTURAL ADHESIVE BONDING PRIMER TECHNOLOGY AND ELECTRODEPOSITION TECHNOLOGY -- Electrodepositable coatings originated as "paints." "Paints" differ from "structural adhesive bonding primers" because of the differences in their functions after application. A "paint" does the following:

*   Provides a decorative coating

*   Provides corrosion protection if so formulated

*   Provides an adequate surface for application of subsequent topcoats.

These functions contrast those for a structural adhesive bonding primer. (See Table 2-1.) Most paints cannot conform to all the requirements listed in Table 2-1; however, proper marriage of the characteristics of

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structural adhesive bonding primers (see Table 2-1) and electodepositable paints (see Section 2.1.3) would have the characteristics described in Table 2-1 and would also:

- Contain a minimal amount of organic solvent since it is primarily water-thinned

- Coat portions of metallic parts that are inaccessible by line-of-sight methods

- Accurately control primer thickness by regulating voltage and bath parameters to maximize bond performance.

2.2   PHASE I: FORMULATION, EVALUATION AND SCREENING

2.2.1   TASK I, STAGE I FORMULATION OF ELECTRODEPOSITABLE PRIMERS -- Prior to the initiation of work under this contract, 3M had spent considerable money and effort to generate a prototype high-temperature performance Cathodic Electrophoretically Depositable Structural Adhesive Bonding Primer (CEDSABP). Therefore, this portion of the program was not concerned with the generation of a CEDSABP, nor with the generation of a formula based upon a lower-temperature performance material. This portion of the program was concerned with the optimization of the prototype formula which had been generated before this research contract began.

A review of the literature regarding electrophoretically depositable primers indicates that there are several generic components with which formulators of such primers are concerned. These components are listed in Table 2-2. Also indicated in Table 2-2 is the function of each major component of an electrophoretically depositable primer. Stage I, Task I of Phase I was concerned with the optimization of the amounts of each of these generic components in a CEDSABP.

The basis for the optimization work was a 2^{6-3} designed experiment. The test matrix for the experiment is shown in Table 2-3. In this fractional factorial design, six components were varied and were evaluated for their

Table 2-2. Generic Components in a Cathodic Electrophoretically Depositable Paint and their Function

GENERIC COMPONENT	FUNCTION
(A) Positively charged film-forming polymer(s)	1. Base component binder 2. Provides physical strength and flexibility
(B) Solubilizing agent for (A)	Makes (A) either water soluble or water dispersible
(C) Crosslinking agent(s)	Insolubilizes and strengthens (A)
(D) Solvents for (A) and (C)	1. Aids processing 2. Aids film formation on cathode
(E) Coalescing solvent(s)	Aids in film formation at the cathode
(F) Pigments	1. Opacification 2. Corrosion inhibition

Table 2-3. Test Matrix for a 2^{6-3} Designed Experiment
for Optimization of the Performance of
3M Prototype CEDSABPs

DESIGN POINT	LEVEL OF VARIABLE					
	A	B	C	D	E	F
1	-	-	-	+	+	+
2	+	-	-	-	-	+
3	-	+	-	-	+	-
4	+	+	-	+	-	-
5	-	-	+	+	-	-
6	+	-	+	-	+	-
7	-	+	+	-	-	+
8	+	+	+	+	+	+

+   Indicates a high level of the variable

-    Indicates a low level of the variable

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effect on the overall performance of the CEDSABP. Variations made to the components included the following:

- The molecular weight of the base polymer

- The level of crosslinking agent based on the weight of the base polymer.

In Table 2-3, the numbers under "Design Point" are the CEDSABP numbers while the letters under "Level of Variable" correspond to the generic component letters in Table 2-2.

The overall quantities of each material used in the generation of the various CEDSABPs are shown in Table 2-4. Table 2-4 shows that the program was modified at midpoint to include a number of other formulas. Two formulas, CEDSABPs 2R and 2RR, were repetitions that were requested by the Air Force on an early candidate for the optimized primer, CEDSABP 2. CEDSABPs 9 and 10 were added as "midpoints" in the designed experiment. CEDSABP 9 was a midpoint with both corrosion inhibiting pigments while 10 was a midpoint without any corrosion inhibiting pigments. CEDSABP 11 was the material chosen as the optimized primer.

A CEDSABP primer is formulated in a number of steps. The first step is the synthesis of a base chemical which is proprietary to 3M. In a second step, this base chemical is reacted with an epoxy resin to provide an epoxy terminated base polymer. The epoxy terminated base polymer is then analyzed for its molecular weight by means of a titration method. The epoxy equivalent weight, which is one-half the molecular weight, is determined by the HCL/pyridine/NaOH titration method. Molecular weights of base polymers ranged from 1034 to 1916, with 1034 considered to be low molecular weight and 1916 considered to be high molecular weight. In a third step, the epoxy terminated base polymer is reacted with either an amine terminating group or a thioether terminating group. In a fourth step, the terminated base polymer is made water compatible by the addition of a water compatibilizing acid. The acid used in our materials

Table 2-4. Design for High-Temperature CEDSABP Optimization

VARIABLE	DESCRIPTION	1 AMOUNT	LEVEL	2 AMOUNT	LEVEL	3 AMOUNT	LEVEL	4 AMOUNT	LEVEL	5 AMOUNT	LEVEL
A	Low Molecular Weight Resin	--		256.8	+	--		256.8	+	--	
	Medium Molecular Weight Resin	--		--		--		--		--	
	High Molecular Weight Resin	295.8	-	--		282.7	-	--		295.8	-
B	Amine Terminating Compound	29.2	-	52.6	-	--		--		29.2	-
	Sulfur Terminating Compound	--		--		38.7	+	53.64	+	--	
	Compatibilizing Acid	25		40.6		28.6		39.54		25	
C	Crosslinker	100.0	-	100.0	-	100.0	-	100.0	-	125.0	+
D	Resin Solvents	150.0	+	100.0	-	100.0	-	150.0	+	150.0	+
E	Coalescing Solvent	100.0	+	50.0	-	100.0	+	50.0	-	50.0	-
F	Chromate Pigment	--		--		37.5	-	37.5	-	37.5	-
	Non-chromate Pigment	121.5	+	121.5	+						
	Pigment Dispersant	22.15		22.2		13.75		13.75		16.25	
	Water (from all sources)	4156.35		4256.3		4299.0		4298.77		4271.25	
	TOTAL	5000		5000		5000		5000		5000	

Table 2-4. Design for High-Temperature CEDSABP Optimization (Cont.)

VARIABLE	DESCRIPTION	6 AMOUNT	LEVEL	7 AMOUNT	LEVEL	8 AMOUNT	LEVEL	9 AMOUNT	LEVEL	10 AMOUNT	LEVEL
A	Low Molecular Weight Resin	256.8	+	--		256.8	+	--		--	
	Medium Molecular Weight Resin	--		--		--		268.2	0	268.2	0
	High Molecular Weight Resin	--		282.7	-	--		--		--	
B	Amine Terminating Compound	52.6	-	--		--		21.93	0	21.93	0
	Sulfur Terminating Compound	--		38.7	+	53.64	+	25.48	0	25.48	0
	Compatibilizing Acid	40.6		28.6		39.54		35.7		35.7	
C	Crosslinker	125.0	-	125.0	-	125.0	-	112.5	+	112.5	0
D	Resin Solvents	100.0	-	100.0	-	150.0	+	125.0	0	125.0	0
E	Coalescing Solvent	100.0	+	50.0	-	100.0	+	75.0	-	75.0	-
F	Chromate Pigment	37.5	-	--		--		25.0	0	0	0
	Non-chromate Pigment	--		121.5	+	121.5	+	95.0	0	0	0
	Pigment Dispersant	16.25		24.65		24.65		23.25		11.25	
	Water (from all sources)	4271.3		4228.85		4128.87		4192.94		4324.94	
	TOTAL	5000		5000		5000		5000 Center Point With Pigments		5000 Center Point Without Pigments	

2-12

Table 2-4. Design for High-Temperature CEDSABP Optimization (Cont.)

VARIABLE	DESCRIPTION	11 AMOUNT LEVEL	12 AMOUNT LEVEL	13 AMOUNT LEVEL	14 AMOUNT LEVEL	15 AMOUNT LEVEL
A	Low Molecular Weight Resin	--				
	Medium Molecular Weight Resin	275				
	High Molecular Weight Resin	--				
B	Amine Terminating Compound	42.3				
	Sulfur Terminating Compound	--				
	Compatibilizing Acid	32.7				
C	Crosslinker	112.5				
D	Resin Solvents	125.0				
E	Coalescing Solvent	75.0				
F	Chromate Pigment	--				
	Non-chromate Pigment	75.0				
	Pigment Dispersant	18.75				
	Water (from all sources)	4243.7				
	TOTAL					

is lactic acid. After the water compatibilizing acid is fully reacted with the base polymer, appropriate solvents are added. The two types of solvents are listed in Table 2-4. The result of the above steps is a brown solution of water compatible polymer.

In a separate step, the corrosion inhibiting pigment and the crosslinking pigment are milled by placing the appropriate amount of pigment and water into a ceramic jar. Ceramic milling media are added as well as a small amount of the above described water compatibilized base polymer which acts as a dispersing aid. The material is milled overnight.

In the next step, the entire contents of the milling jar are added to the solution of the water compatibilized base polymer. Further adjustments are made in the amount of water and solvent in the material to provide a primer that is approximately 40 percent solids. This primer concentrate is the product material.

The primer concentrate must be carefully diluted to a concentration of about 10 percent solids for use. The concentrate is placed in a container that is equipped with an air driven motor that is attached to a paddle type stirrer, preferably a "high-lift" stirrer. Distilled or deionized water is added slowly to the primer concentrate to "let it down." Too rapid addition of the water will cause the primer to coagulate. There is a point (break-point) during the addition of water at which the viscosity of the primer rapidly decreases. After the break-point, water may be added rapidly. The primer is a beige to light-yellow dispersion which will settle in a few days if it is not agitated.

2.2.2   SUBSTRATES AND ADHESIVES -- The specification for high-temperature resistant adhesive bonding of honeycomb sandwich constructions for the F-111 is General Dynamics specification FMS-1013B. This specification calls for 2024-T81 bare aluminum as face sheets and 5052 aluminum as the core material. The tests designed to probe the performance of the CEDSABP are listed in Table 2-5 while the design criteria are listed in Table 2-6. In the tests described in Tables 2-5 and 2-6, the aluminum sheet was 2024-T81 bare aluminum. The surface of

2-14

Table 2-5. Test Description

PERFORMANCE PARAMETER	DESCRIPTIVE PARAGRAPH OR SPECIFICATION	NUMBER OF SPECIMENS OR RUNS	COMMENTS
1. Deposition Characteristics		One at each voltage 10v, 20v, 30v, 40v, 50v, 60v	None
2. Throwpower		One at optimum voltage determined in 1	Honeycomb core is 1/2" thick, 3/8" cell size
3. Film Properties		One at each voltage determined in 1	Thickness determined by Isometer, pencil hardness
4. Peel Properties	ASTM D3167-76	2	None
5. Shear Properties	MMM-A-132 (Paragraph 4.4)	3 at each temperature	None
6. High Temperature Resistance	MMM-A-132 (Paragraph 4.4)	3 at each exposure temperature	None
7. Flatwise Tension	ASTM C197-61	2 at each temperature	Both core and face sheet electroprimed. Honeycomb core is 1/2" thick, 3/8" cell size
8. Corrosion Resistance of Shear Specimens	MMM-A-132 (Paragraph 4.4)	3	None
9. Film Corrosion Resistance	ASTM B-117	2	None
10. Bath Stability		One gallon sample	Sample kept in sealed container and stirred on roller mill for 30 days
11. Solvent Resistance		1	Resistance to 50 back and forth rubs with methyl ethyl ketone

Table 2-6. Performance Criteria for CEDSABP Optimization Program

PERFORMANCE CHARACTERISTICS	DESIGN CRITERIA
1. Deposition Characteristics	1. Film deposits at voltages less than 60 V and exhibits current drop characteristics.
2. Throwpower	2. Uniformly coats entire depth of 0.5" thick core.
3. Film Properties	3. Cured film deposits at approximately 0.1 mil and visually uniform.
4. Peel Properties	4. Room temperature floating roller peel is unaffected by presence of primer.
5. Shear Properties	5. -65°F, room temperature, 325°F, 350°F shear properties are unaffected by presence of primer.
6. High Temperature Resistance	6. Exposure of lap shear specimens to 350°F for 200 hours shows minimum effect on shear strength when tested at 325°F.
7. Flatwise Tension	7. Flatwise tension when measured at room temperature and 325°F is unaffected by presence of primer.
8. Corrosion Resistance of Shear Specimens	8. Minimum drop in RT shear strength after 30-day salt spray exposure.
9. Film Corrosion Resistance	9. Minimum creep from scribe and minimum blistering after 30-day salt spray exposure.
10. Bath Stability	10. Minimum effect on properties 1, 2, 3, and 6 (above) after 30 days at room temperature, stirred.
11. Solvent Resistance	11. No rub-off with methyl ethyl ketone.

the aluminum was prepared according to Boeing specification BAC 5555 and is described in Table 2-7. The honeycomb core used in this work was made of 5052 alloy and was not corrosion resistant. The honeycomb core was also anodized according to the process described in Table 2-7. Care was taken to make attachments to the core in such a fashion that current would flow through the entire core; thus, the attachments could only be made at the end of the core parallel to the ribbon direction.

Titanium alloy (Ti-6Al-4V) was also used in the optimization experiments. The surface preparation was the 5-volt chromic acid anodization process as described in Table 2-8. The complete set of tests, as described in Tables 2-5 and 2-6, were not run using titanium; rather, only lap shear properties were determined (Tests 5 and 6, Table 2-6). Measurements on titanium were limited to those tests because of the unavailability of equipment to machine titanium at 3M.

The adhesive used in the optimization work was AF-143. This adhesive was chosen because it was the adhesive used under Air Force Contract F33615-80-C-5069. With the choice of this adhesive, it was possible to compare the optimization results directly with those obtained under Contract F33615-80-C-5069.

2.2.3 **TEST RESULTS** -- In the following paragraphs, test results which were used to optimize the primer formulation are described. Each test is discussed individually below but the entire data package is included in Appendix A.

2.2.3.1 **Apparatus Description** -- A schematic of the electrochemical apparatus used for the determination of deposition characteristics is shown in Figure 2-2. The equipment shown in Figure 2-2 is also the equipment used for all of the CEDSABP work performed at 3M under this contract. The CEDSABP is placed in a glass tank equipped with a pump and heat exchanger. These were added during the time frame of this contract since it was found that pumping gave better suspension of pigments than the use of a stirrer. The heat exchanger was added to keep the temperature of primer near room temperature to reduce loss of solvent by

Table 2-7. Phosphoric Acid Anodization Process

Alkaline Degrease

Oakite 164 (180°F), 10 minutes

Cold Water Dip

Cold Tap Water Rinse, 2 minutes

Optimized FPL Etch (155°F), 10 minutes

DI Water Rinse, 2 minutes

Phosphoric Acid Anodization

3.1 N

Room Temperature

15V for 22.5 minutes

DI Water Rinse, 5 minutes

Air-Dry, 10 minutes

Forced Air-Dry (155°F), 10 minutes

Prime Parts within 72 hours

Table 2-8. Titanium Surface Preparation

(5V Chromic Acid Anodization)

Alkaline Degrease

Oakite 164 (180°F), 10 minutes

Tap Water Rinse, 2 minutes

Nitric-hydrofluoric Acid Etch, 90 seconds

0.85 liter conc. nitric acid

0.12 liter 48% hydrofluoric acid

0.11 gram FC-95

Dilute to 2 liters with distilled water

Tap Water Rinse, 2 minutes

Chromic Acid Anodization

97.6 grams Chromic Acid

Dilute to 2 liters with distilled water

6 milliliters hydrofluoric acid

5 V, Room Temperature, 20 minutes

DI Water Rinse, 5 minutes

Forced Air-Dry (150°F), 10 minutes

Prime Parts within 48 hours
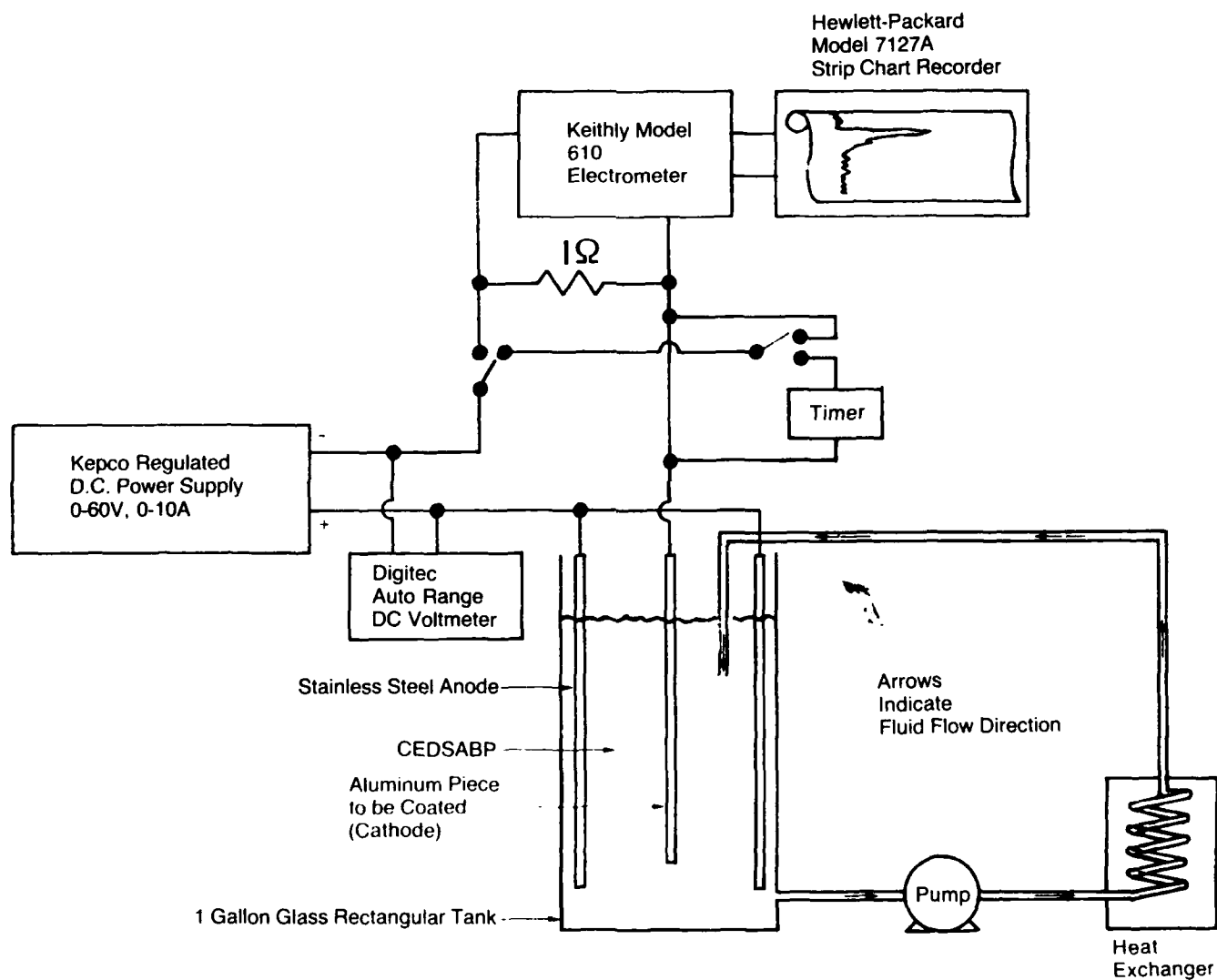
Figure 2-2. Apparatus for Determination of Deposition Characteristics
and for Deposition of CEDSABPs

evaporation and reduce heat history. In addition, the plastic plumbing used in this apparatus was changed during the course of the contract. The original plumbing was Tygon^R tubing. We found that substantial amounts of solvent can be lost by evaporation through the tubing. Replacement of the Tygon^R tubing with polypropylene eliminated this problem. One additional modification was made to the apparatus during the course of this contract; a timing circuit was added that allowed 3M to better reproduce deposition times.

2.2.3.2   Aging Test -- One goal of the program was to provide some data regarding the life of the CEDSABP under use conditions. Because of time limitations, a test had to be generated which might be considered predictive of the life of the primer. The test we picked was to place the primer in a sealed container and place that container on a roller mill for a month. Several properties of the primer were determined before and after this aging test.

2.2.3.3   Deposition Characteristics -- The key features of an electrophoretically depositable paint in comparison to a spray paint are discussed in Paragraph 2.1.1. In order to obtain optimum deposition characteristics, certain criteria must be met:

- Voltages necessary to obtain the proper OH^- level for deposition must be low enough to be industrially feasible.

- Deposition time must be short.

- Current drop must be rapid to indicate the insulating character of the deposited film.

These parameters can be determined directly or indirectly by an electrochemical method. The deposition characteristic experiment was carried out in the following fashion. A voltage is set on the Kepco power supply and is monitored by the calibrated Digitec voltmeter. An aluminum panel of dimension (1-inch x 0.5-inch x 0.020-inch) that had been surface prepared as described in Table 2-7 is placed in the CEDSABP. A switch is thrown and the current draw is measured by monitoring the

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voltage across a 1-ohm resistor. The output of the electrometer is displayed on a strip chart recorder, and current time curves are measured as a function of several applied voltages. Current time curves that are exemplary of those taken in this work are shown in Figure 2-3. This figure shows curves taken on CEDSABP 6 as a function of applied voltage. The characteristic time for each curve is taken to be the time at which the current reaches 1/e (1/2.718) of its maximum value with short 1/e times considered to be good.

The deposition time results, as a function of CEDSABP, are plotted in Figure 2-4. These results were obtained for primers that were freshly formulated. Essentially all of the primers provide short 1/e times at voltages, in excess of 30V. However, several CEDSABPs provide short 1/e times at 20V or less. These primers are 1, 2, 2R, 5, 8, 9, and 11.

The deposition properties of the CEDSABPs were one of the set of parameters determined after 1 month of aging on a roller mill. These results are plotted in Figure 2-5. The deposition characteristics of the primers change substantially with this aging test. Samples 2RR, 3, 4, 6, 7, and 8 show essentially unusable deposition characteristics after the aging process. CEDSABPs 1, 2, 2R, 5, 9, 10, and 11 show little change in their deposition characteristics after aging.

2.2.3.4   Throwpower -- Throwpower is a term used to describe the ability of a CEDSABP to coat portions of parts that are inaccessible by line-of-sight methods. The current time curves shown in Figure 2-3 are indicative of the throwpower of a CEDSABP. A CEDSABP having poor deposition characteristics will also likely have poor throwpower. A functional throwpower test was also performed. A 1/2-inch thick phosphoric acid anodized core was coated with each CEDSABP. A CEDSABP completely coating the core was considered to have good throwpower.

Throwpower results are listed descriptively in Table 2-9. Before aging, CEDSABPs 1, 2, 2R, 2RR, 5, 6, 9, 10, and 11 all provide reasonable throwpower at low voltages. These are the same materials which

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Applied Voltage

10 V. ————
20 V. – – – –
30 V. ⋯⋯⋯⋯
40 V. –·–·–·–

Current (Arbitrary Units)

Time (sec)
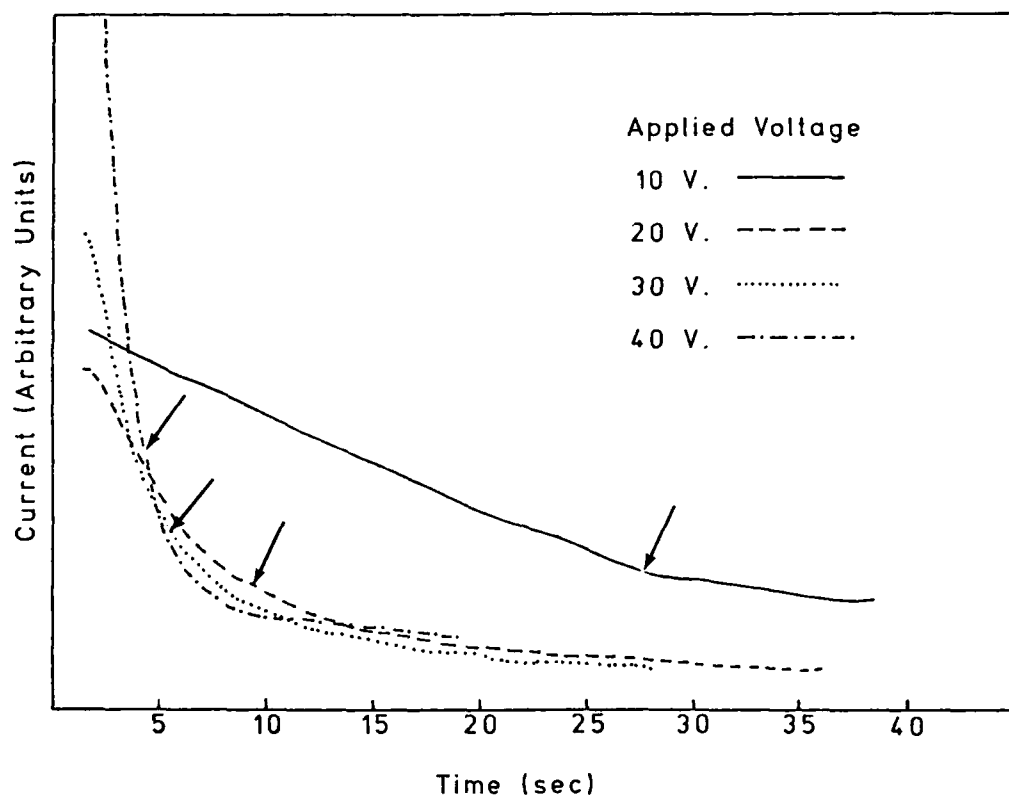
(Arrows indicate the 1/e times)

Figure 2-3. Current Drop Curves as a Function of Voltage for CEDSABP 6

CEDSABP Optimization
Phos. Anod. Aluminum, Current Drop
Characteristics. INITIAL
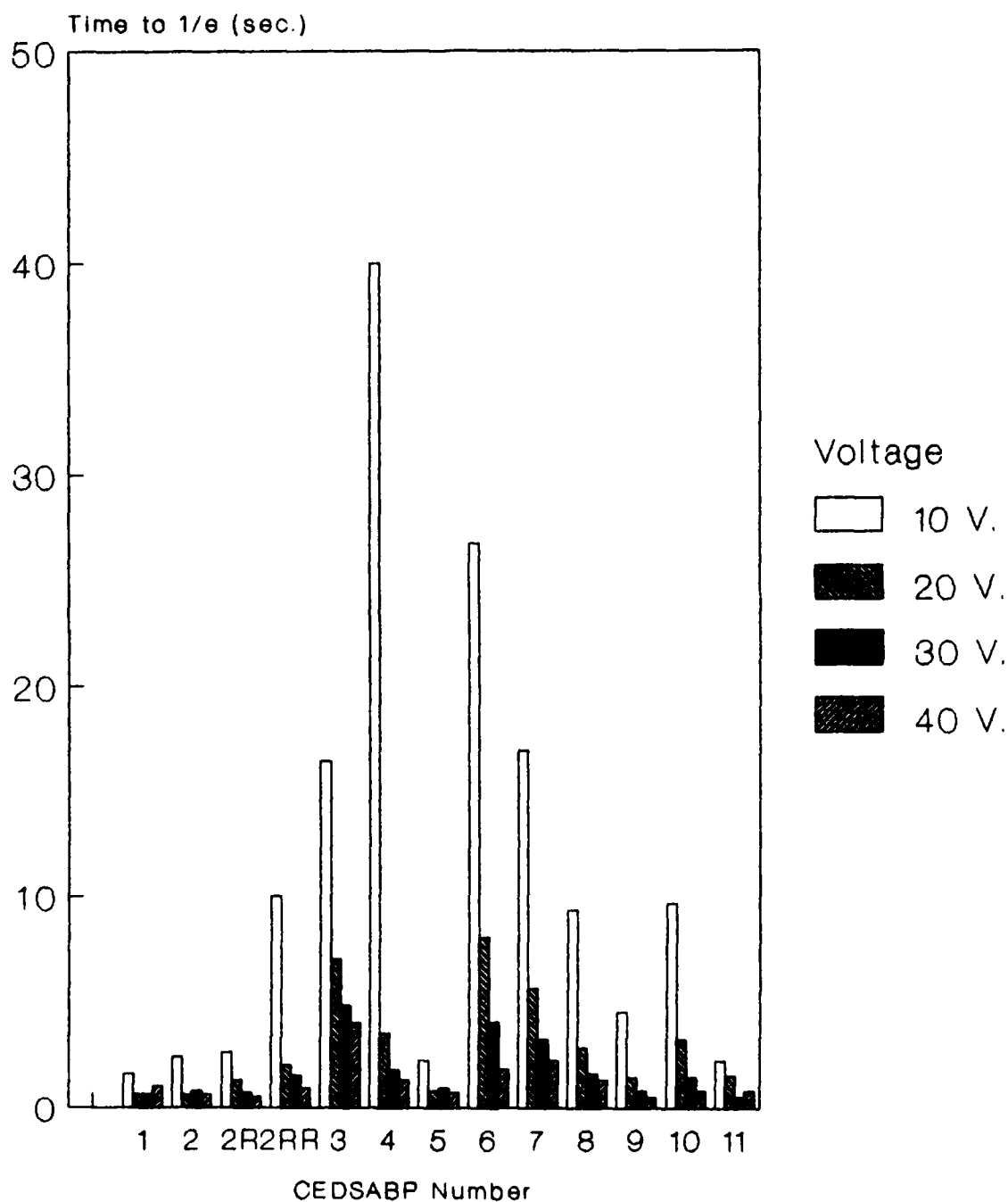
Figure 2-4. CEDSABP Optimization, Current Drop Characteristics, Initial

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CEDSABP Optimization
Phos. Anod. Aluminum, Current Drop
Characteristics. After Aging
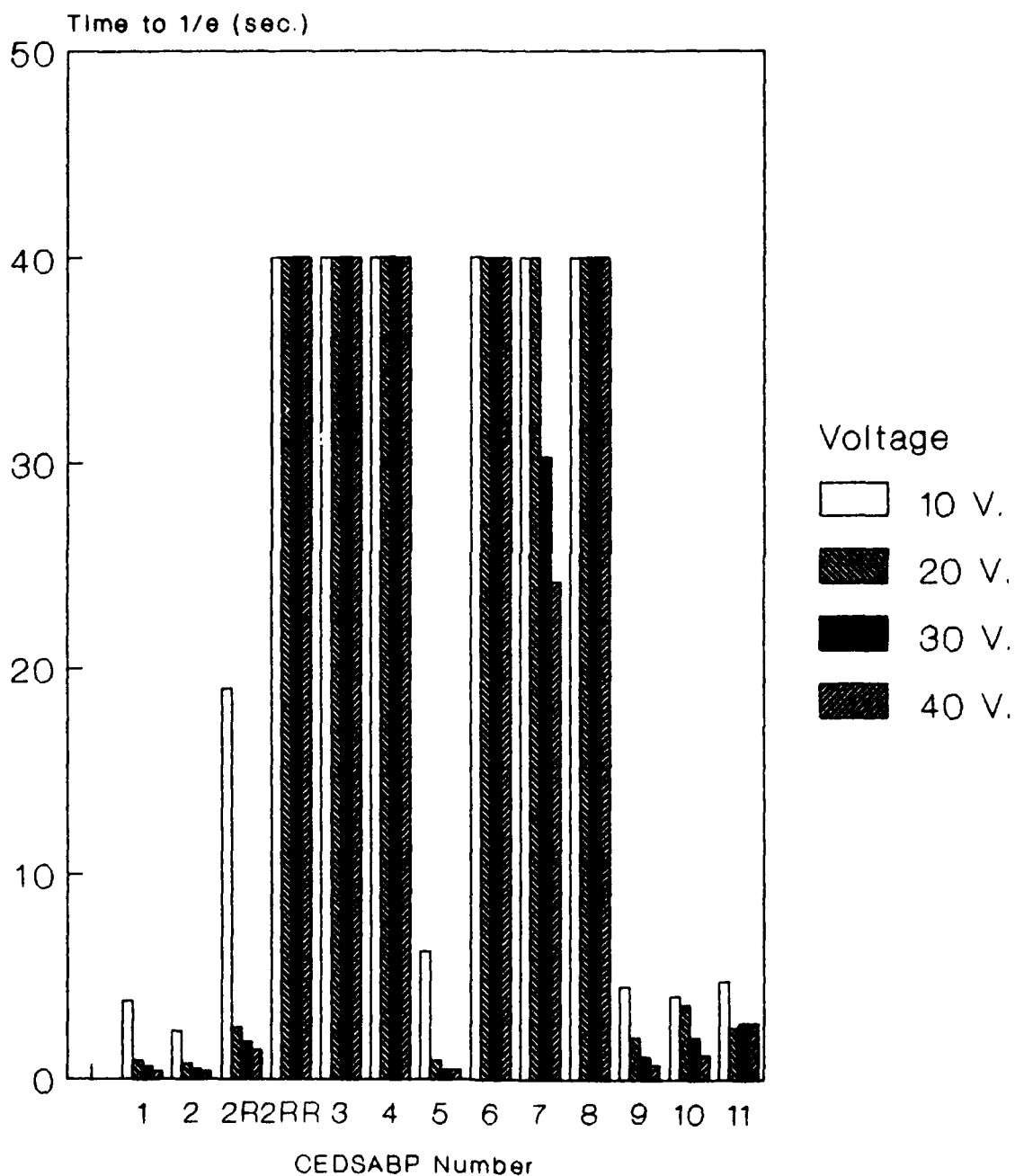
Figure 2-5. CEDSABP Optimization, Current Drop Characteristics, after 30 Days of Aging on Roller Mill

Table 2-9. Throwpower

(Coating of 1/2-inch Thick Honeycomb Core)

CEDSABP NO.	BEFORE AGING	AFTER AGING
1	Complete at 20-30V	Complete at 40V
2	Complete at 20-30V	Complete at 20-30V
2R	Complete at 20-30V	Incomplete at 60V
2RR	Complete at 20V	Incomplete at 20-30V
3	Incomplete at 60V	Incomplete at 60V
4	Incomplete at 60V	Incomplete at 60V
5	Complete at 20-30V	Complete at 40V
6	Complete at 20-30V	Agglomeration
7	Incomplete at 60V	Incomplete at 60V
8	Incomplete at 60V	Incomplete at 60V
9	Complete at 20-30V	Complete at 40V
10	Complete at 20-30V	Complete at 30V
11	Complete at 30V	Complete at 20-30V

demonstrate good current drop characteristics. Table 2-9 also lists the throwpower after the 30-day aging test. The CEDSABPs which provide good throwpower after aging are 1, 2, 5, 9, 10, and 11. This corresponds well to the current drop characteristics described above.

Typically, poor throwpower results in coating of the core only at the edges where the potential drop is the highest. Also, poor throwpower results in coatings that are loosely adhered before cure and appear to have many pinholes.

2.2.3.5 Film Properties -- Flat sheets of phosphoric acid anodized aluminum were electrodeposited with each of the CEDSABPs as a function of deposition voltage. The CEDSABP was then cured for 2 hours at 350°F. The film thickness was determined at a number of locations on each of the panels by means of an Isometer. A positive film property characteristic is linear or quasilinear increase of film thickness with deposition voltage. An alternative positive characteristic is little or no increase in film thickness with increasing voltage, which is indicative of excellent throwpower. In addition, the visual appearance of the coating was monitored. Coatings that are rough, cratered, or otherwise visually defective were considered to have negative characteristics. The cured coatings were checked for hardness by means of scratching the surface with a hard pencil. A coating with lack of resistance to scratching with a pencil of at least 6H hardness was considered to have negative characteristics.

The thickness and pencil hardness characteristics of each CEDSABP coating are shown in Appendix A. All of the CEDSABPs provide 9H pencil hardness before and after aging. Before aging, CEDSABPs 1, 5, 8, 10, and 11 provided linearly increasing primer thickness; 2, 2R, 2RR, and 9 seemed to provide a limiting thickness; and 3, 4, 6, and 7 provided thick coatings. After aging, CEDSABPs 1, 2, 2R, and 11 seemed to provide a limiting thickness; CEDSABP 9 provided linearly increasing film thickness; and the remainder of the primers provided thick coatings.

The visual appearance of the coatings is listed in Table 2-10. Before aging, all of the coatings provided smooth semi-gloss or glossy coatings except for 3, 7, and 8. These coatings were thick on the edges or had a pebbly appearance. After aging, the appearance of many of the coated, cured CEDSABP films changed markedly. All of the CEDSABPs experienced some change in the appearance except for 1, 2, 10, and 11. Slight changes were observed for 5 and 9.

2.2.3.6   Solvent Resistance -- As discussed in Paragraph 2.1.5, a CEDSABP must exhibit resistance to aircraft fluids. The normal test for such resistance involves immersing lap shear bonds in various aircraft fluids and noting performance changes as a function of time in the fluid. Instead of the immersion test, a rapid test for this type of performance was used for faster evaluation of the primer. This test is a standard coating test and involves rubbing the cured CEDSABP surface with a cheesecloth soaked with methyl ethyl ketone (MEK). A positive performance characteristic is the lack of removal of the CEDSABP with 50 back-and-forth rubs.

All of the CEDSABPs, before and after aging, provided resistance to the MEK rub test after a cure of 2 hours at 350°F.

2.2.3.7   Physical Properties -- Most of the tests listed under Items 5, 6, and 7 in Table 2-6 are physical properties' tests of adhesive bonds made with adherends primed with various CEDSABPs. The tests are described in the specifications listed in Table 2-5 and will not be repeated here.

EC-3917 was selected as the control primer. It is a solvent-base corrosion inhibiting primer that has been used in the aerospace industry for over 20 years and is a 3M standard primer for use with high-temperature epoxy adhesives. All of the data regarding physical performance of adhesive bonds made using CEDSABPs are compared to the performance of bonds made using adherends primed with EC-3917. The EC-3917 was applied at a thickness of about 0.0001-inch and cured for 1 hour at 350°F.

Table 2-10. Coating Quality

CEDSABP NO.	ATTRIBUTE	BEFORE AGING	AFTER AGING
1	Texture Color Uniformity	Slightly rough Light brown Thin, uniform	Less rough More yellow Thin, uniform
2	Texture Color Uniformity	Very slightly rough Light brown Thin, uniform	Very slightly rough Light brown Thin, uniform
2R	Texture Color Uniformity	Semi-gloss Light brown Thin, uniform	Rough, pebbly Brown Thin in spots
2RR	Texture Color Uniformity	Semi-gloss Light brown Thin, uniform	Rough, pebbly Yellow brown Thick on edges. Washes off.
3	Texture Color Uniformity	Pebbly Yellowish Thin, non-uniform (edge)	Very pebbly Brown Incomplete
4	Texture Color Uniformity	Glossy Yellowish Thin, uniform	Very pebbly Browner Incomplete
5	Texture Color Uniformity	Glossy Yellowish Thin, uniform	Somewhat rougher Slightly browner Uniform, slightly pebbly
6	Texture Color Uniformity	Slightly pebbly Yellow brown Thin, uniform	Agglomeration
7	Texture Color Uniformity	Glossy Yellowish Non-uniform (edges)	Pebbly Yellowish Thick, esp. edges
8	Texture Color Uniformity	Glossy Yellowish Slightly thick on edges	Pebbly Browner Thick on edges
9	Texture Color Uniformity	Glossy Light brown Thin, uniform	Semi-gloss Browner Thin, uniform
10	Texture Color Uniformity	Glossy Light brown Thin, uniform	Glossy Yellowish Thin, uniform
11	Texture Color Uniformity	Semi-gloss Light brown Thin, uniform	Semi-gloss Yellow brown Thin, uniform

The raw data regarding the adhesive bond tests are shown in Appendix A. The codes for the apparent failure modes of each specimen are as follows:

CP   = Cohesion Failure in the Primer Layer

CA   = Cohesion Failure in the Adhesive

AP, APM = Apparent Adhesion Failure, Primer to Metal

APA   = Apparent Adhesion Failure, Primer to Adhesive

The APM and APA failure modes are listed as "apparent" since detailed surface analysis was not performed, and only a visual appraisal of the type of failure was made.

Figures 2-6 through 2-9 show the values for metal-to-metal adhesive bond shear strength for aluminum adherends primed with the CEDSABPs generated under this program. In general, the values of bond strength are in the range expected for AF-143 on aluminum at the test temperatures. In these figures and Appendix A, we show a comparison to the control "C" which was obtained using the AF-143/EC-3917 adhesive/primer system. The horizontal dark line on each figure corresponds to the control strength. The dashed lines on each figure correspond to a standard deviation around the control strength. The standard deviation which we normally obtain for lap shear specimens is ±200 psi. As shown in Figures 2-6 through 2-9, the lap shear strengths of all of the CEDSABPs except CEDSABP 3 fall well within the range of the standard deviation of the control values and in some cases exceed this range. In Figure 2-9, a number of the CEDSABPs (3, 7, 8, 9, and 10) do not have 350°F lap shear strengths which fall into the standard deviation of the control. The results are very close, and with the same size of standard deviation applied to these numbers, the range of standard deviations easily overlaps. CEDSABP 11 meets or exceeds the performance of the control in all cases. Figure 2-10 shows that all of the CEDSABPs give results most equivalent to the control value with aging for 200 hours at 350°F. This is an important result, since this is the property which the primer developed under Contract F33615-80-C-5069 could not provide. The failure surfaces for the bonds made with aluminum adherends are also listed in Appendix A.
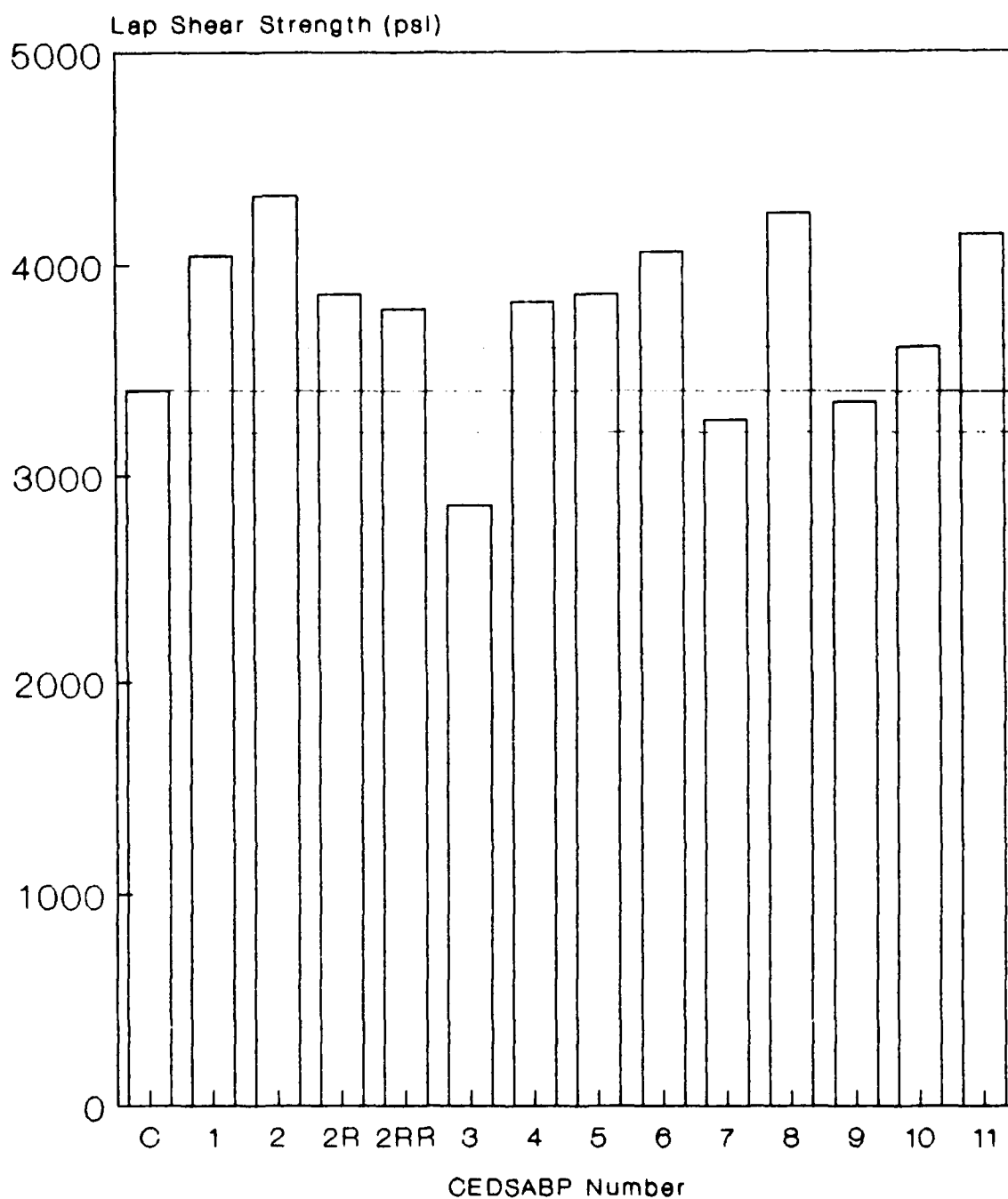
Figure 2-6. CEDSABP Optimization, AF-143/Phosphoric Anodized 2024-T81, -67°F Lap Shear Strength
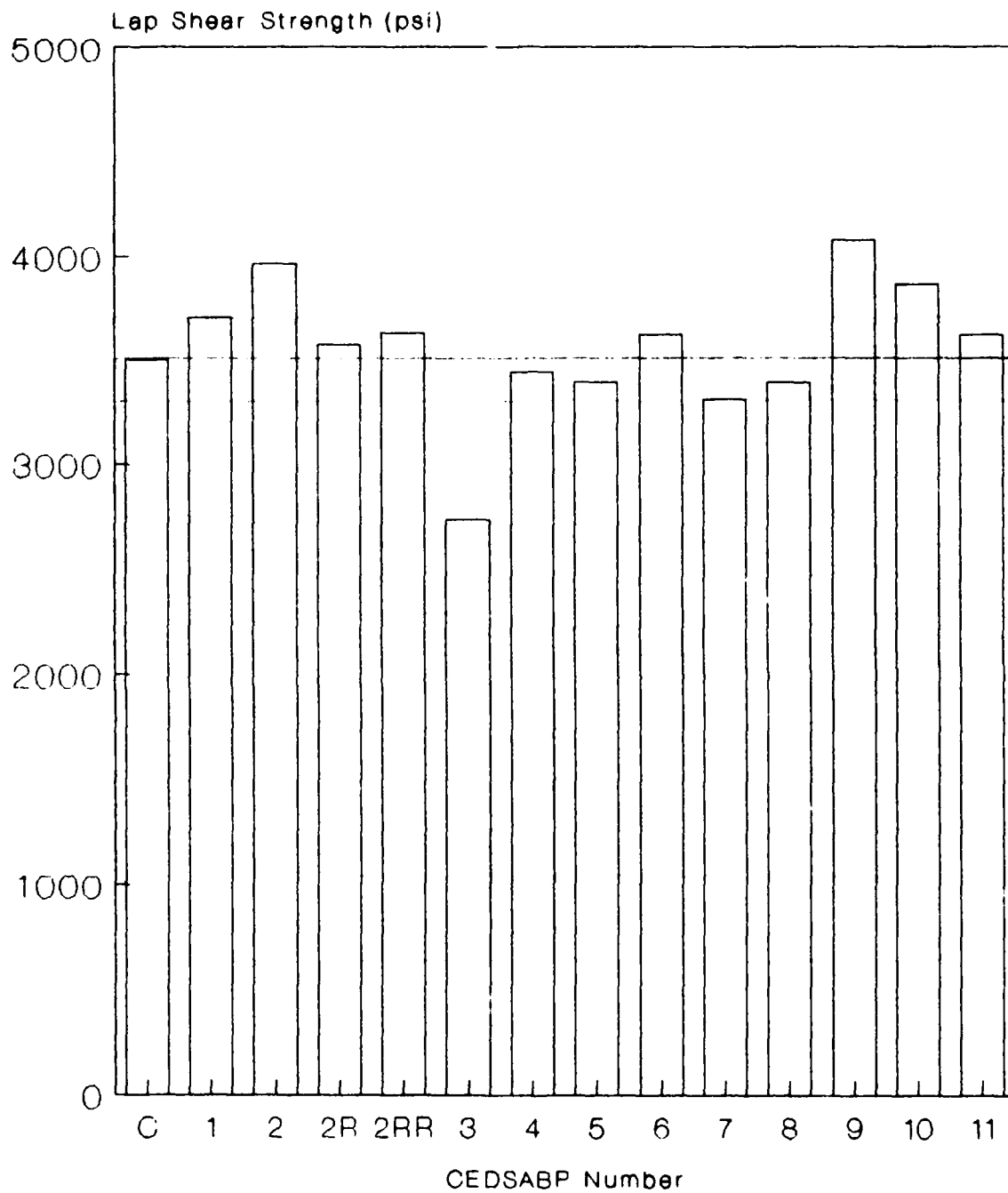
Figure 2-7. CEDSABP Optimization, AF-143/Phosphoric Anodized 2024-T81, RT Lap Shear Strength
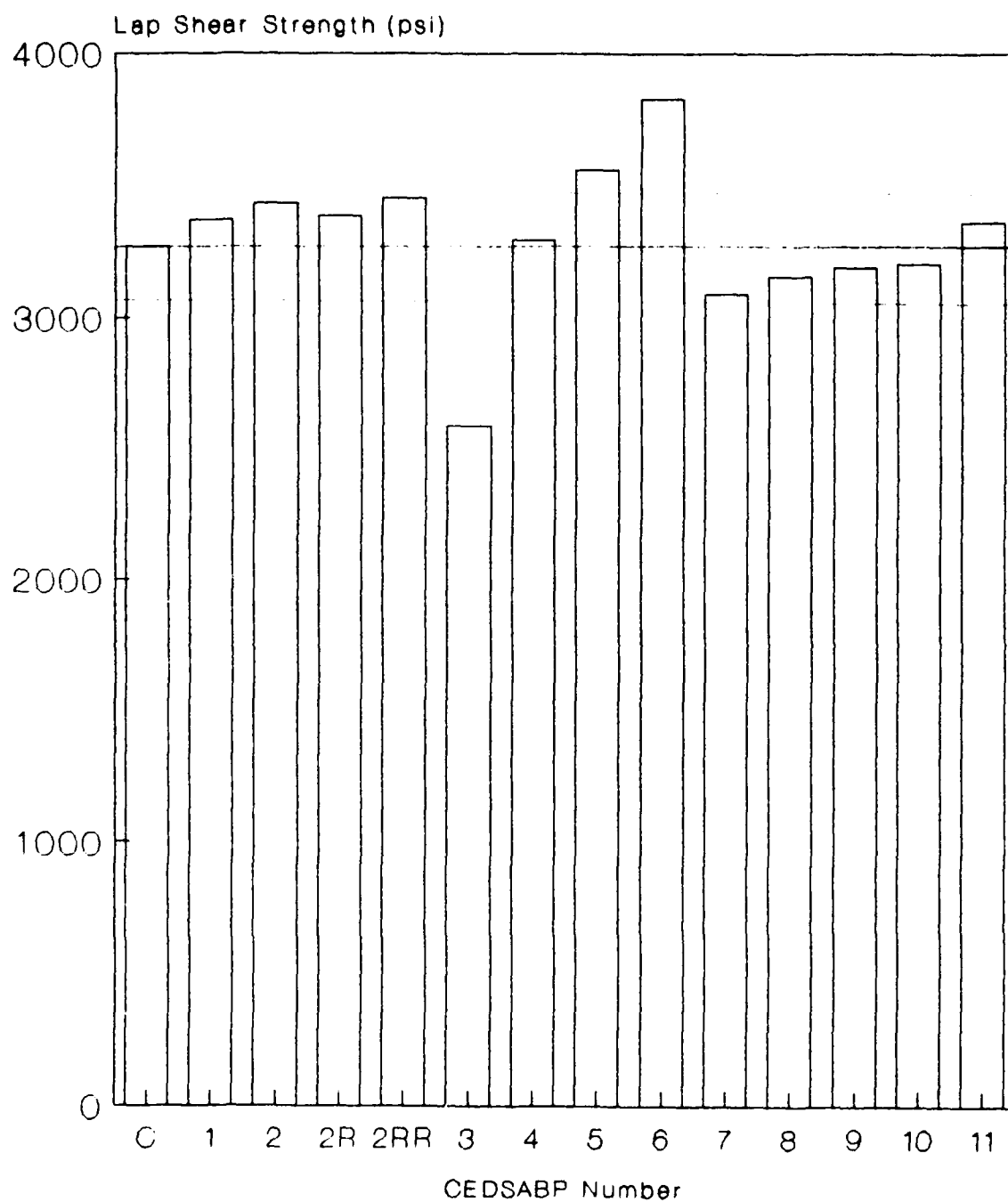
Figure 2-8.   CEDSABP Optimization, AF-143/Phosphoric Anodized 2024-T81, 325°F Lap Shear Strength
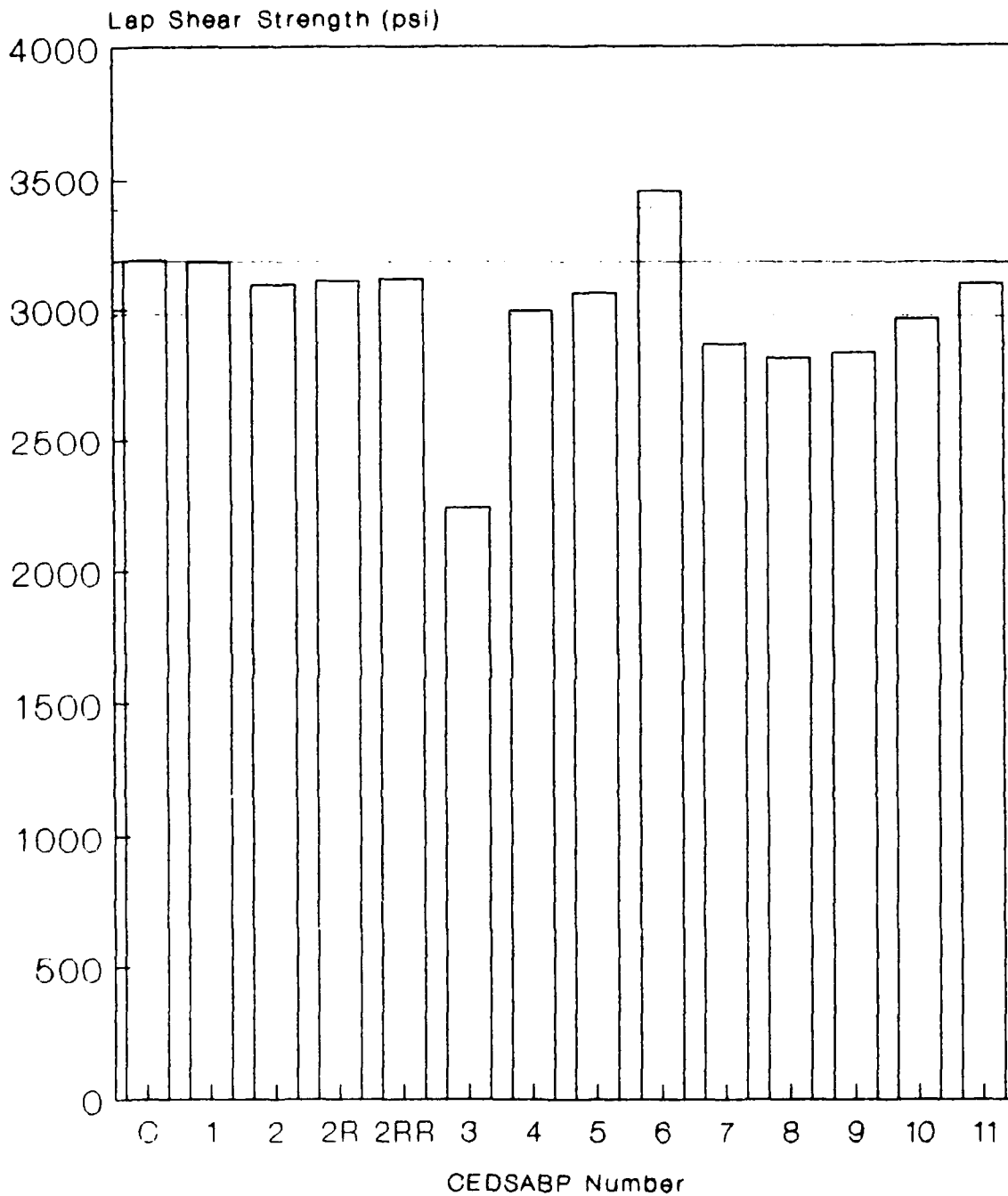
Figure 2-9. CEDSABP Optimization, AF-143/Phosphoric Anodized 2024-T81, 350°F Lap Shear Strength
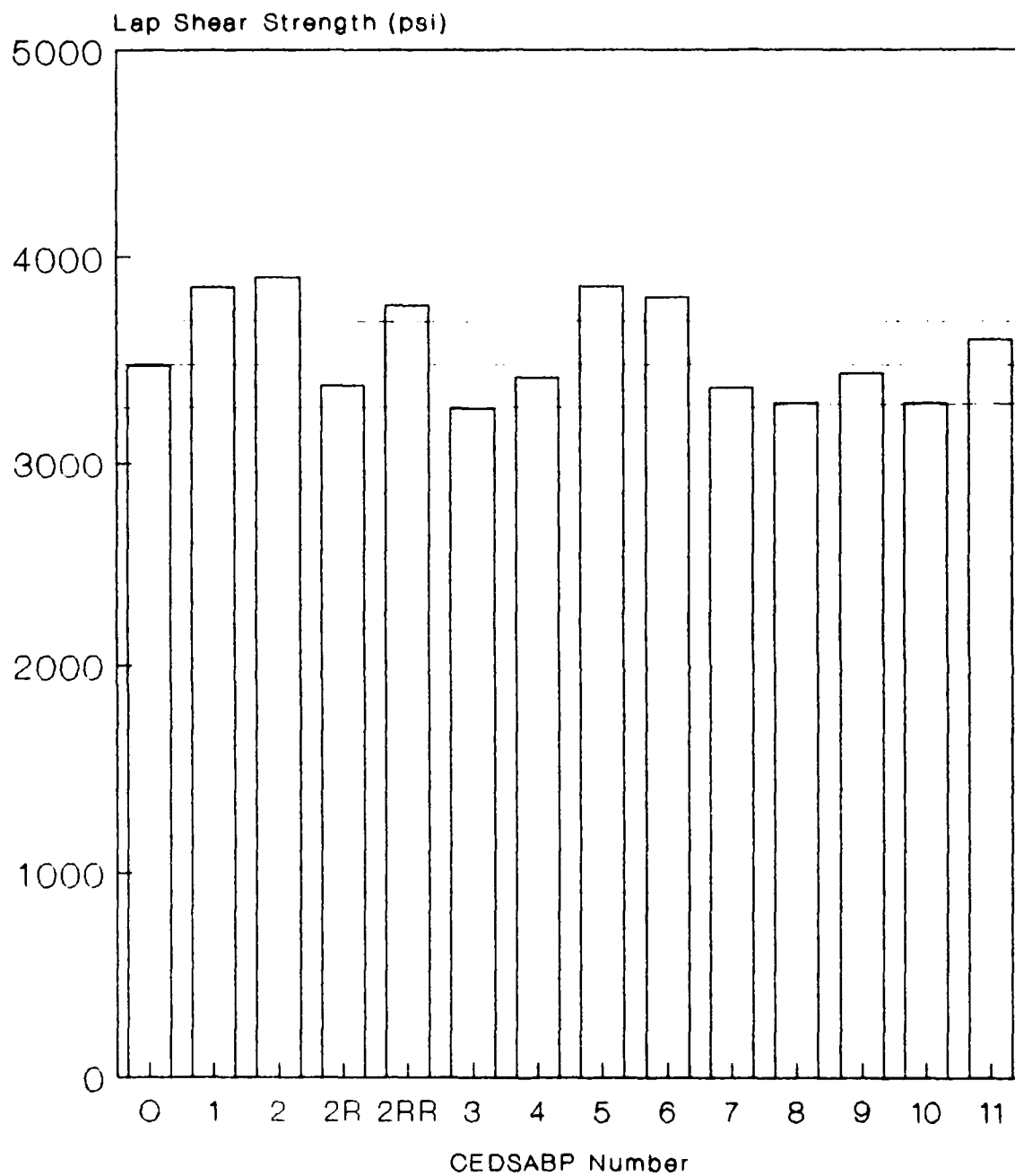
Figure 2-10. CEDSABP Optimization, AF-143/Phosphoric Anodized 2024-T81, 320°F Lap Shear after 200 Hours at 350°F

The failure is generally cohesion failure within the adhesive for bonds tested at room temperature and at elevated temperatures. The failures, however, are mixed cohesion failure in the adhesive, and cohesion failure in the primer at -67°F.

Flatwise tension results are shown in Figure 2-11. We do not have an accurate estimate of the standard deviation of this test; however, Figure 2-11 does show that all of the CEDSABPs easily exceed the control strength at 325°F. The only CEDSABP which gives distinctly inferior performance on all of the aluminum tests is CEDSABP 3. The cause for this is unknown but may be related to the poor deposition characteristics of this CEDSABP. Overall, except for the case of CEDSABP 3, the physical strength characteristics of adhesive bonds made with adherends primed with CEDSABPs are not very sensitive to the chemical composition of the CEDSABP.

The bond strengths that were obtained under this program using titanium adherends are shown in the Appendix A and in Figures 2-12 through 2-15. The values are in the range expected for this adhesive on titanium. Once again, the CEDSABP results can be compared to the set of EC-3917/AF-143 standards. The control strengths and standard deviation are shown in each figure. The results show that the lap shear numbers are far more variable than they are for aluminum. This is especially true at low temperatures. At higher temperatures, CEDSABPs 1, 2, and 11 seem to provide the best results in comparison to the control, and the results are far less variable than they are at low temperatures. As with the bonds on aluminum, the bonds tested at higher temperatures show cohesion failure in the adhesive; however, at lower temperatures, such as room temperature and -67°F, the failures are either a mixed cohesion failure in the adhesive and primer, or cohesion failure in the oxide. The cohesion failure in the oxide is much more prevalent at -67°F. This apparent cohesion failure in the oxide is determined visually in that the metal adherend appears to be shiny metal instead of the colored rough oxide. The shear numbers at low temperature seem to correspond to the amount of oxide removed; the more oxide removed, the lower the shear strength. It is possible that the 5-volt chromate acid anodize may not

2-36
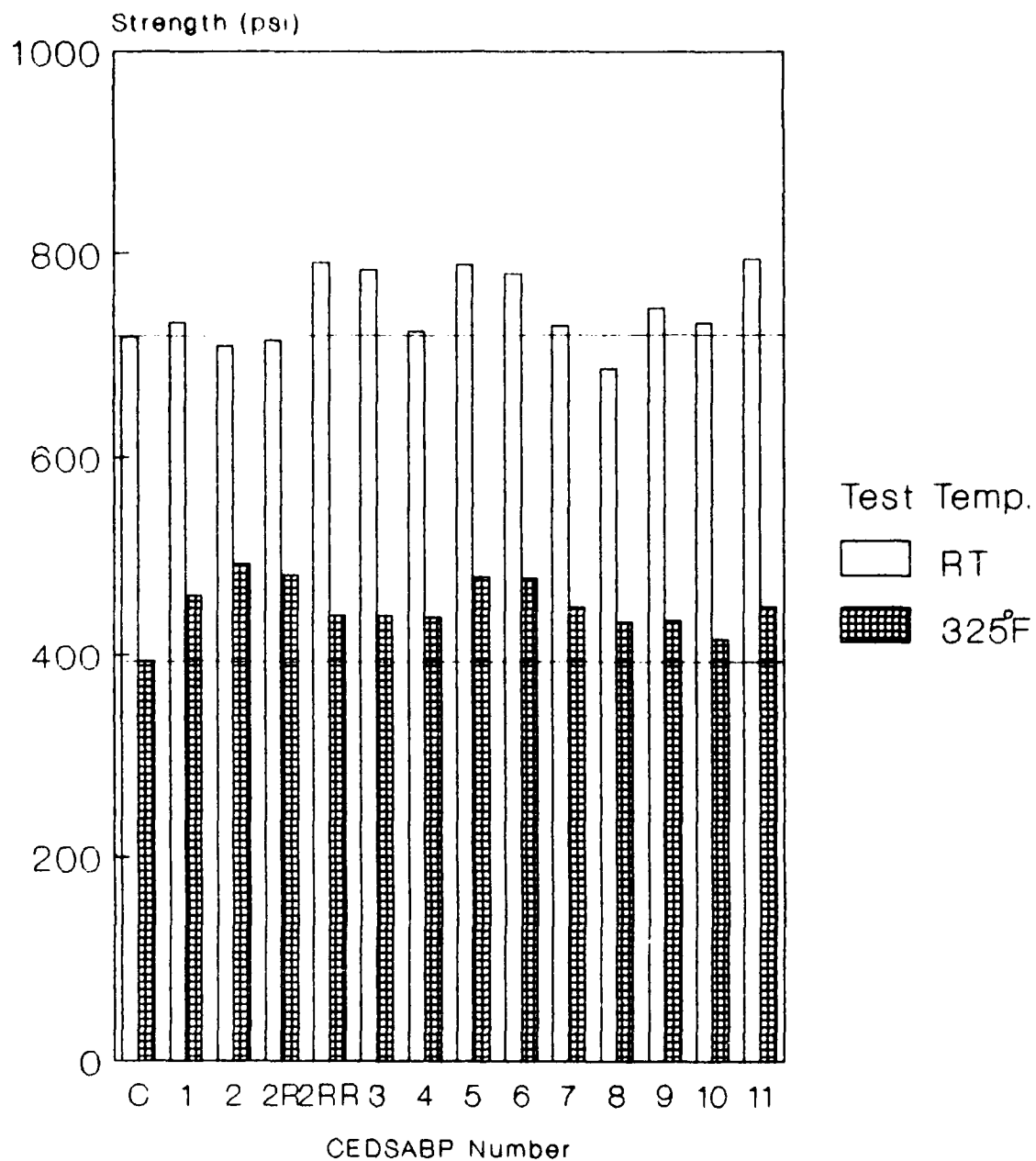
Figure 2-11.   CEDSABP Optimization, AF-143/Phosphoric Anodized Aluminum,
Flatwise Tension
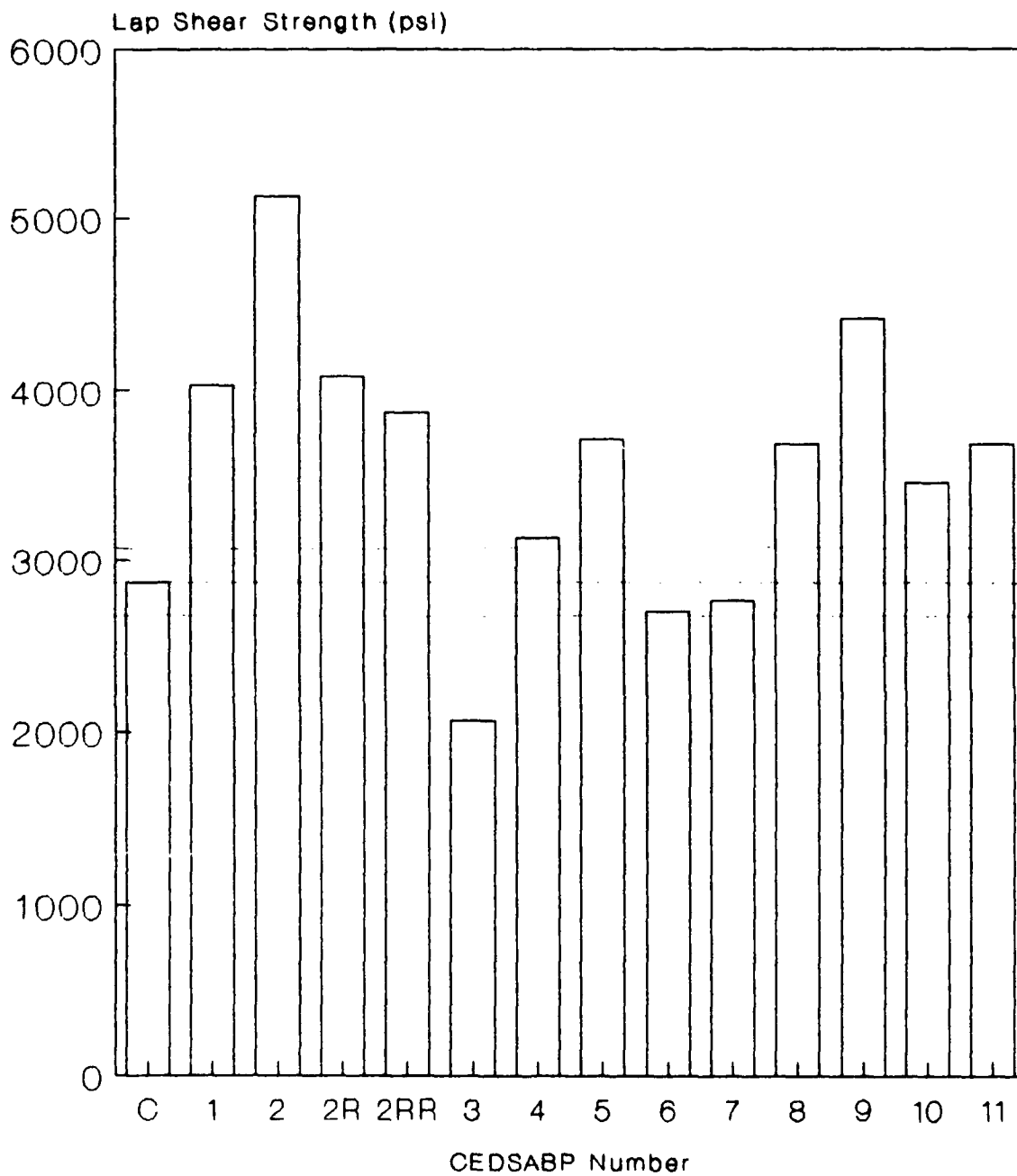
Figure 2-12. CEDSABP Optimization, AF-143/Chromic Acid Anodized Titanium, -67°F Lap Shear Strength
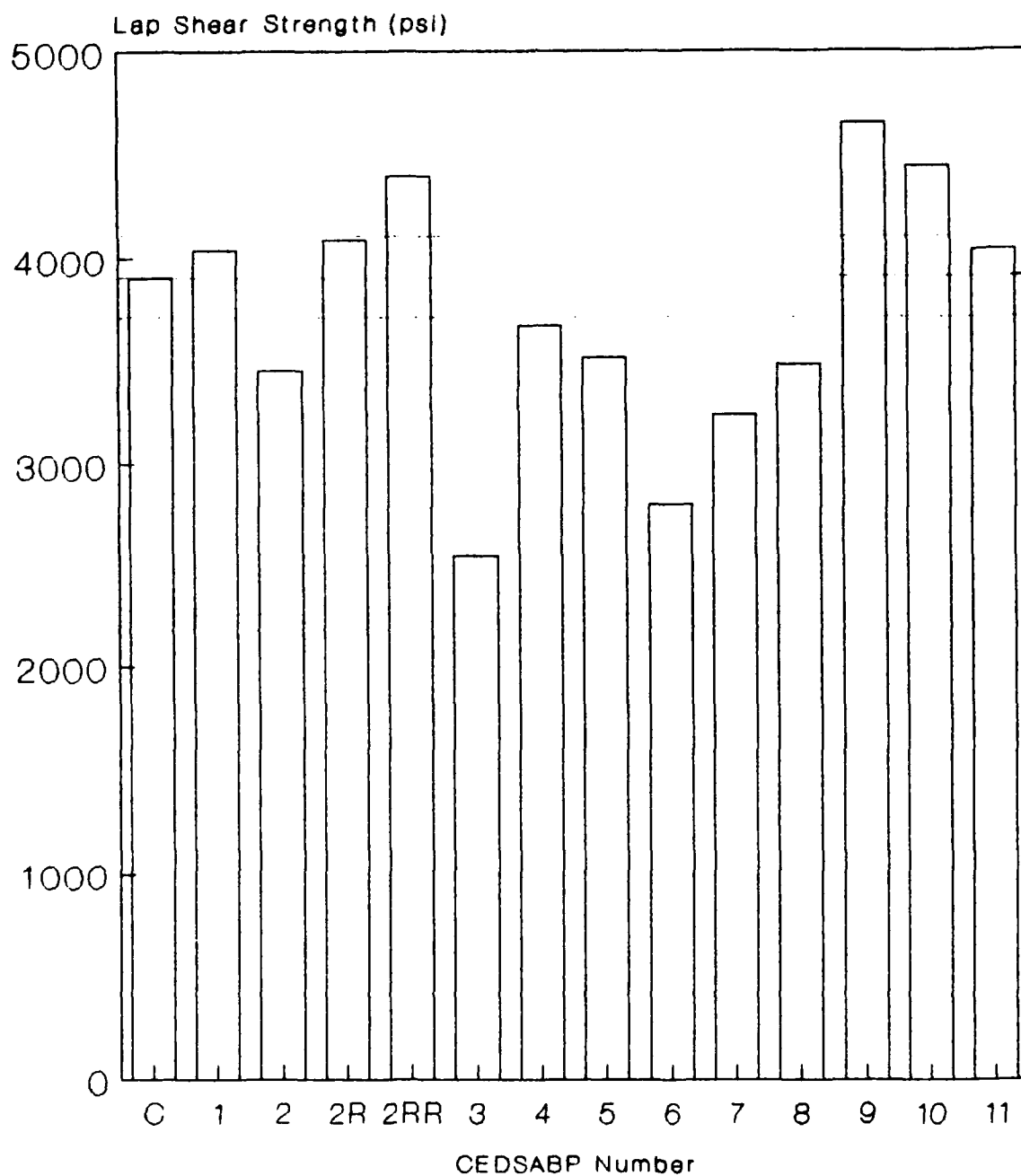
Figure 2-13. CEDSABP Optimization, AF-143/Chromic Acid Anodized Titanium, RT Lap Shear Strength
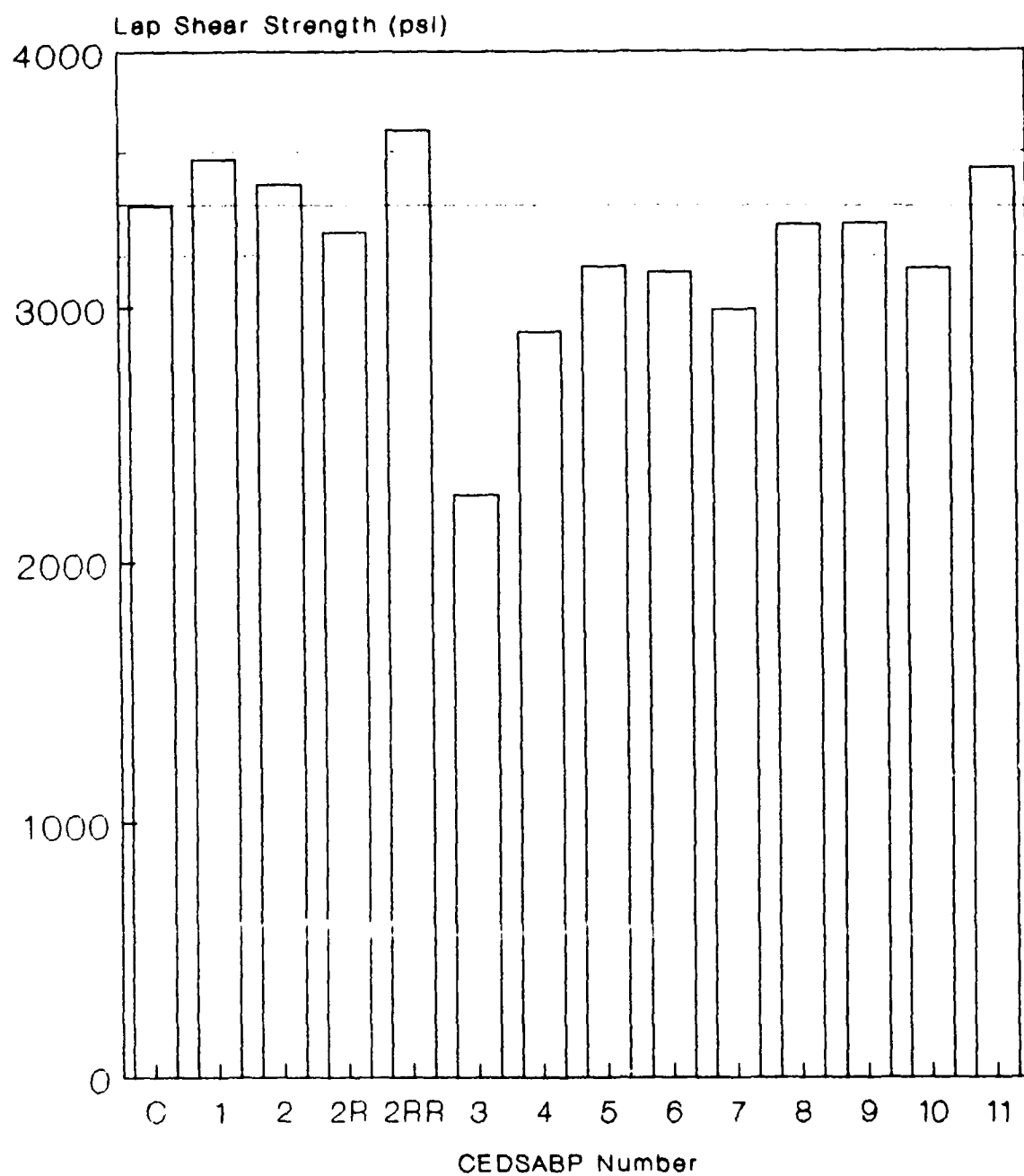
Figure 2-14.   CEDSABP Optimization, AF-143/Chromic Acid Anodized Titanium, 325°F Lap Shear Strength
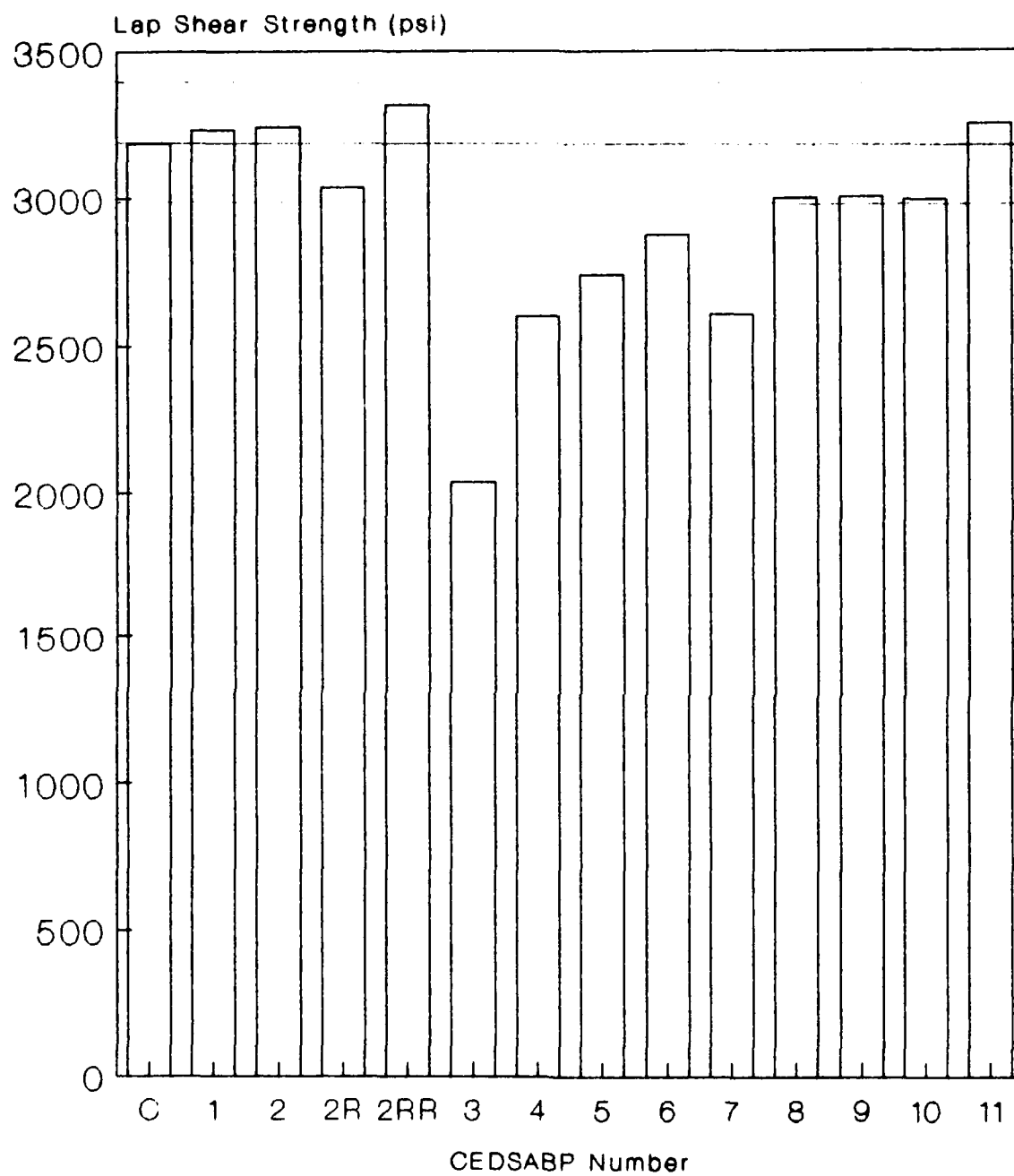
Figure 2-15. CEDSABP Optimization, AF-143/Chromic Acid Anodized Titanium, 350°F Lap Shear Strength

be the best surface preparation for the acceptance of a CEDSABP. For the most part, the strength results for the CEDSABPs are acceptable. CEDSABP 11 particularly gave a performance that met or exceeded that of the control. The result of the 350°F heat soak was also positive for most of the CEDSABPs, as shown in Figure 2-16.

2.2.3.8   Environmental Exposure -- During this task, several environmental exposure simulation conditions were used. The first of these was to expose lap shear specimens to salt spray conditions for 30 days and determine the decrease in lap shear strength after that exposure. The salt fog environment was generated according to ASTM B-117. The results of salt fog exposures are shown in Figure 2-17 and are also listed in Appendix A. With the exception of CEDSABP 4, the failures were all cohesion failure in the adhesive and no visible undercutting caused by corrosion was observed.

The second type of environmental exposure was what we term "facial" corrosion exposure. In this test, panels were generated for each CEDSABP having primed and cured coatings of a thickness of about 0.0001-inch. The "face" of the panel was scribed with an "X" by means of a sharp razor blade. The panel was then exposed to 30 days of salt fog controlled as prescribed by ASTM B-117. The panels were placed in a wooden holder which kept the face of the panel at a 7° tilt from vertical to ensure that the panel face was constantly subjected to salt fog without shading from other panels. Table 2-11 gives the results of the facial salt fog tests. After 30 days of salt fog exposure, the samples primed with the various CEDSABPs showed no evidence of corrosion under the coating, with the exception of CEDSABPs 2RR and 10. CEDSABP 10 did not actually display corrosion under the coating; rather it displayed a small amount of pitting corrosion which probably formed at defects in the coating. The greatest portion of the surface of the panel coated with CEDSABP 10 was uncorroded. Pits were also apparent on panels coated with CEDSABPs 3 and 7, but were not as apparent as those on the panel coated with CEDSABP 10. The pits on panels coated with CEDSABPs 3 and 7 could also have been just coating defects, because they are not nearly as visible as those on the panels coated with CEDSABP 10. CEDSABP 10 does not

2-42
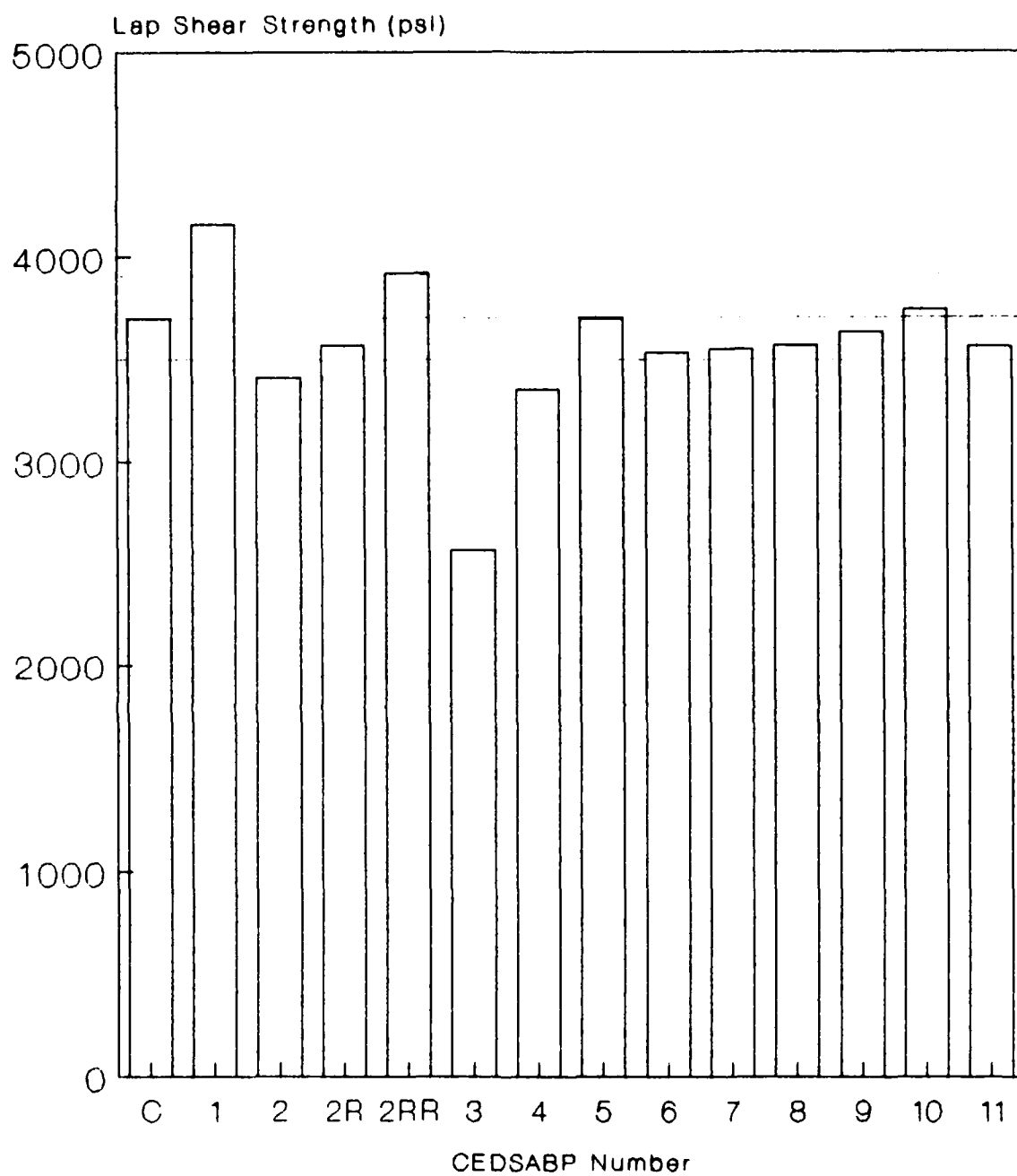
After 200 Hours at 350°F

Figure 2-16. CEDSABP Optimization, AF-143/Chromic Acid Anodized Titanium, 320°F Lap Shear after 200 Hours at 350°F
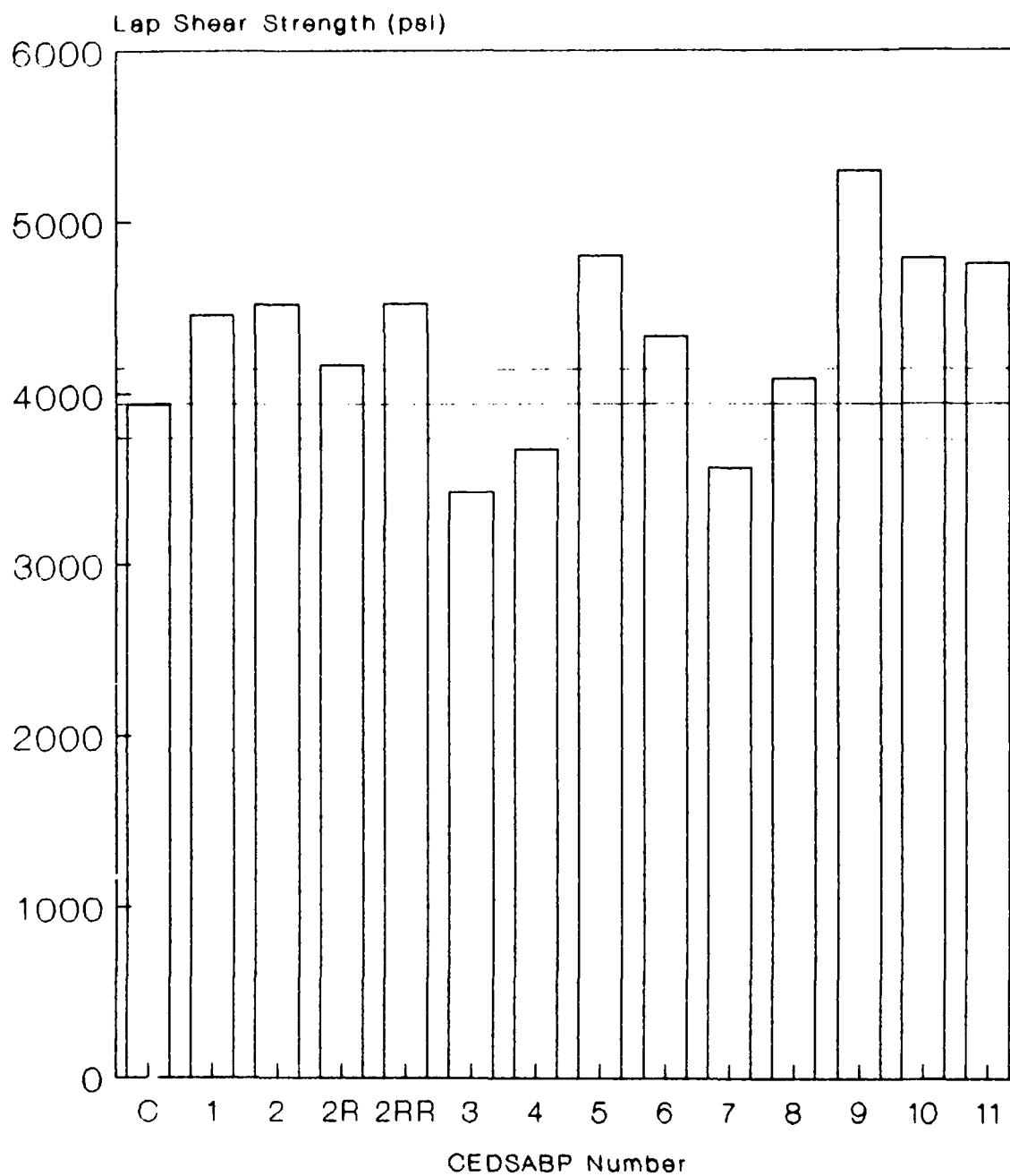
After 30 Days Salt Spray Exposure

Figure 2-17. CEDSABP Optimization, AF-143/Phosphoric Anodized 2024-T81, RT Lap Shear after 30 Days of Salt Fog

Table 2-11. Facial Corrosion Resistance

CEDSABP NO.	BLISTERS	CREEP FROM SCRIBE	SCRIBE CORROSION	PITS	DRIP MARKS	PEELING UP
3917	60 percent of panel surface is completely corroded					
1	No	No	Slight	No	Yes	No
2	No	No	Slight	No	Yes	No
2R	No	No	Slight	No	Yes	No
2RR	No	No	Slight	Yes	Yes	No
3	No	No	Slight	Maybe	No	No
4	No	No	No	No	No	No
5	No	No	No	No	No	No
6	No	No	Slight	No	Slight	No
7	No	No	No	Maybe	No	No
8	No	No	No	No	Slight	No
9	No	No	No	No	No	No
10	No	No	No	Slight	Slight	No
11	No	No	Slight	No	Slight	No

contain any corrosion-inhibiting pigment and therefore does not have any mechanism to hinder corrosion other than barrier properties; so once the corrodant breached the coating, there was no other mechanism to impede its progress. In general, the salt fog results indicate that the CEDSABPs containing non-chromate corrosion-inhibiting pigments were slightly less effective than those which contained chromates, since the coatings containing chromate had no blister formation within the scribes while those with non-chromate corrosion-inhbiting pigments had some blisters. CEDSABP 2RR displayed general corrosion on one of the panels that was exposed to this test; however, the other panel coated with 2RR did not show this corrosion. We can only assume that the panel was in some way improperly coated or surface treated.

The important comparison of the above described results is made with panels coated with EC-3917. This primer has been used effectively in the aerospace industry for over 20 years. The EC-3917 panels showed very poor corrosion protection compared to the CEDSABP coated panels. EC-3917 is heavily loaded with chromate based corrosion inhibiting pigments, but the CEDSABPs, even CEDSABP 10, showed orders of magnitude in better performance than did EC-3917. We conclude that this must be due to the better barrier properties of a CEDSABP versus a spray-applied primer.

2.2.3.9 Bath Stability in Aging -- The screening test for bath stability was discussed above. Of the CEDSABPs that were generated, the best overall retention of coating performance was obtained with CEDSABPs 10 and 11. The test results of CEDSABPs 2, 2R and 2RR, which were supposedly of the same formulation, did not agree. This was a matter of great concern, but the structure of the program did not allow us to delve into this difference too deeply. Some preliminary investigations of changes in CEDSABP 2R were made. Qualitatively, we found that the usual resin solvent odor had decreased and that the conductivity had changed markedly. Experiments were done which demonstrated that with dialysis and solvent replenishment, most of the throwpower returned. CEDSABPs will increase in conductivity with use because of the liberation of the

water-compatibilizing acid during the deposition step; however, during this type of aging experiment, the CEDSABP was not used, so the conductivity increase must have come from a different source. The most likely source is slow dissolution of the corrosion inhibiting pigment. CEDSABP 10 was formulated to evaluate the effect of corrosion inhibiting pigment, and the coating characteristics of CEDSABP 10 were the least affected by the aging experiment. This seems to indicate that the culprit is the corrosion inhibiting pigment. We believe that this is the reason why ultrafiltration is practiced in the electrophoretic priming industry. (See Section 6, Item 5.) Ultrafiltration is believed to be a form of dialysis.

CEDSABP 11 provided excellent retention of throwpower and coating characteristics after aging. The formulary of CEDSABP 11 was achieved by examining the data for the preceding CEDSABPs and finding trends which seemed to give better stability.

Even though the coating characteristics had changed for many of the CEDSABPs, the high-temperature strength results after high-temperature aging of adhesive bonds (using primer that had been aged on the roller mill for 30 days) were almost the same as those shown in Figures 2-18 and 2-19. This indicates that strength characteristics are not the only major criterion for a proper CEDSABP coating.

2.2.4   CONCLUSIONS FROM PHASE I, TASK I, STAGE I -- In the original proposal for this contract, the optimized CEDSABP was to be generated by the results of a computer analysis of the variance of the data generated above. Later, permission was sought to eliminate this computer analysis from the program because (1) there was not enough variation in the strength results, and (2) all of the sulfur-terminated base resins gave poor performance. Thus, half of the data necessary to complete the 2^{6-3} design were negative. This did not provide enough information to act
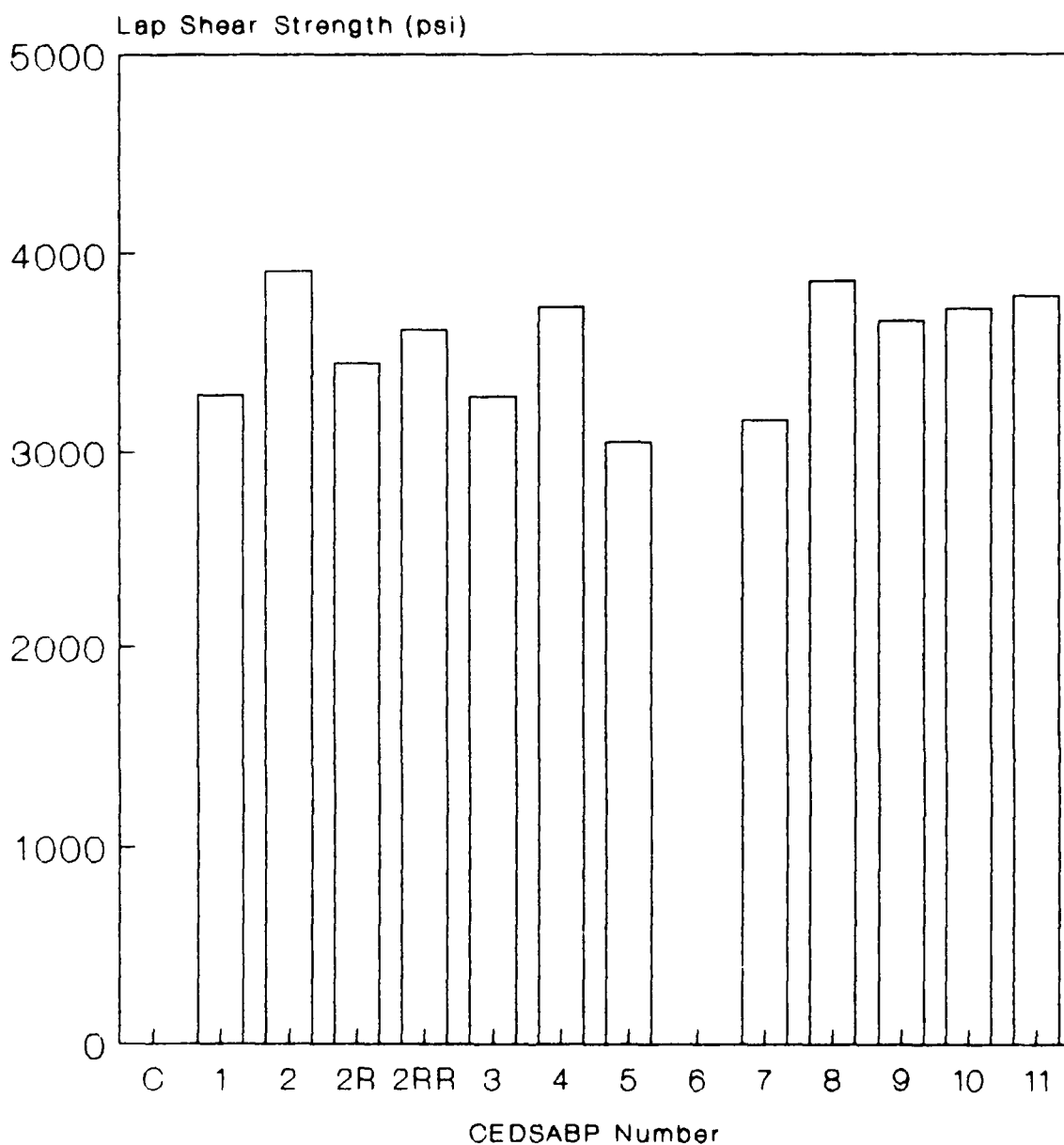
Primer Applied After 30 Days Roller Mill
Bond Strength Tested after 200 Hrs at
350°F

Figure 2-18. CEDSABP Optimization, AF-143/Phosphoric Anodized 2024-T81,
325°F Lap Shear after 200 Hours at 350°F

Figure 2-19. CEDSABP Optimization, AF-143/Chromic Acid Anodized Titanium, 325°F Lap Shear after 200 Hours at 350°F

upon the programs; rather, it was decided that the obvious trends in the data could be used to generate the optimized CEDSABP. Such trends were:

- Amine termination gives far superior throwpower and coating quality in comparison to sulfur termination.

- Molecular weight has a small effect on coating quality; however, higher molecular weight base resins are very difficult to handle in the processing steps.

- CEDSABPs need a corrosion inhibiting pigment to decrease the possibility of pit formation at coating defects.

- The corrosion inhibiting pigment should be non-chromated to comply with pollution control laws in California.

- There was no clear effect as to the level of crosslinker and solvent; however, solvent is lost during use and this does affect the coating characteristics. This indicates the need for close monitoring of solvent levels during use.

- Retention of throwpower seemed to be the key problem; this seems to be related to:

  - The presence of a corrosion inhibiting pigment

  - The molecular weight of the resin (higher molecular weight seems less affected).

- Throwpower can be returned with proper dialysis and replenishment procedures.

The above conclusions forced the choice of the formulary of CEDSABP 11 which has:

- A medium molecular weight base resin

- A non-chromate corrosion inhibiting pigment

- A lower level of corrosion inhibiting pigment

- Amine termination

- Solvent levels commensurate with molecular weight of the base resin.

2.3   PHASE I, TASK I, STAGE II - CEDSABP PROCESS DEVELOPMENT REPLENISHMENT METHODS, QUALITY CONTROL AND EVALUATION AGAINST GOVERNMENT SPECIFICATIONS

2.3.1   ADHESIVE SELECTION -- In the choice of adhesive, our intent was to use an adhesive that has been qualified to FMS-1013B. The 3M Adhesive, AF-130, was qualified to this specification and considered for use, but production of AF-130 was discontinued because of its asbestos content, and we were not able to use the actual adhesives qualified to this specification. Instead, the data generated during Stage II of Phase I, Task I wcs generated, using a number of different adhesives. The adhesives were all high-temperature resistant mater.als, and designated as follows: AF-143, AF-131, and AF-131-2. AF-131-2 is considered an asbestos-free replacement for AF-130.

2.3.2   CEDSABP SELECTION -- The criteria for the formulation of the CEDSABP were discussed above. During this stage, 3M found that the level of solvent was too low in CEDSABP 11 to provide for proper coating of anodized titanium; therefore, the solvent level was increased to accomplish this. The material with increased solvent level, but otherwise identical to the formulary of CEDSABP 11, was given the 3M

product designation of XA-3995. Table 2-12 compares the formulary of CEDSABP 11 and XA-3995.

2.3.3   REPLENISHMENT METHOD -- The replenishment method study was revised to include the determination of the depletion rate of the primer bath. This was accomplished by coating panels to deplete the solids in XA-3995. This was done over several month's time period and is discussed below.

Analytical tests were run at an interval more convenient to the altered program. These results are discussed below, as well as the analytical tests developed to examine XA-3995 as a function of use.

2.3.4   BATH LIFE -- The XA-3995 bath was monitored by a number of analytical techniques during its use in Phase I, Task I, Stage II. These analytical methods were:

- Particle Size Analysis by Means of a Coulter Counter
- Resin Analysis via High-Performance Liquid Chromatography
- Solvent Analysis using Gas Chromatography
- Acid Content via pH
- Total Ionic Content via Conductivity
- Pigment Analysis via Gravimetric Analysis
- Deposition Characteristics
- Strength of Adhesive Bonds.

Each of the above techniques will be discussed in the following paragraphs.

2.3.4.1   Particle Size Analysis by Means of the Coulter Counter -- In this method, a small amount of XA-3995 is added to a salt water solution. The salt water solution is deaerated and stirred and a Coulter Counter head is placed in the dispersion. A particle size distribution of differential population percent versus particle size is obtained. A plot is shown in Figure 2-20 where the particle size distribution is plotted versus the age of the primer. The laboratory-generated lot of XA-3995

Table 2-12. Final Formulations

VARIABLE	DESCRIPTION	CEDSABP 11	XA-3995
A	Low MW Resin Medium MW Resin High MW Resin	254.0	245.0
B	Amine Term Cmpd Sulfur Term Cmpd	34.1	39.3
C	Compatibilizing Acid	26.32	30.2
D	Resin Solvents	116.0	187.2
E	Coalescing Solvent	70.0	118.1
F	Chromate Pigment Non-Chromate Pigment	67.5	67.5
	Pigment Dispersant	16.7	16.9
	Water From All Sources	4314.0	4194.0
	Total	5000.0	5000.0
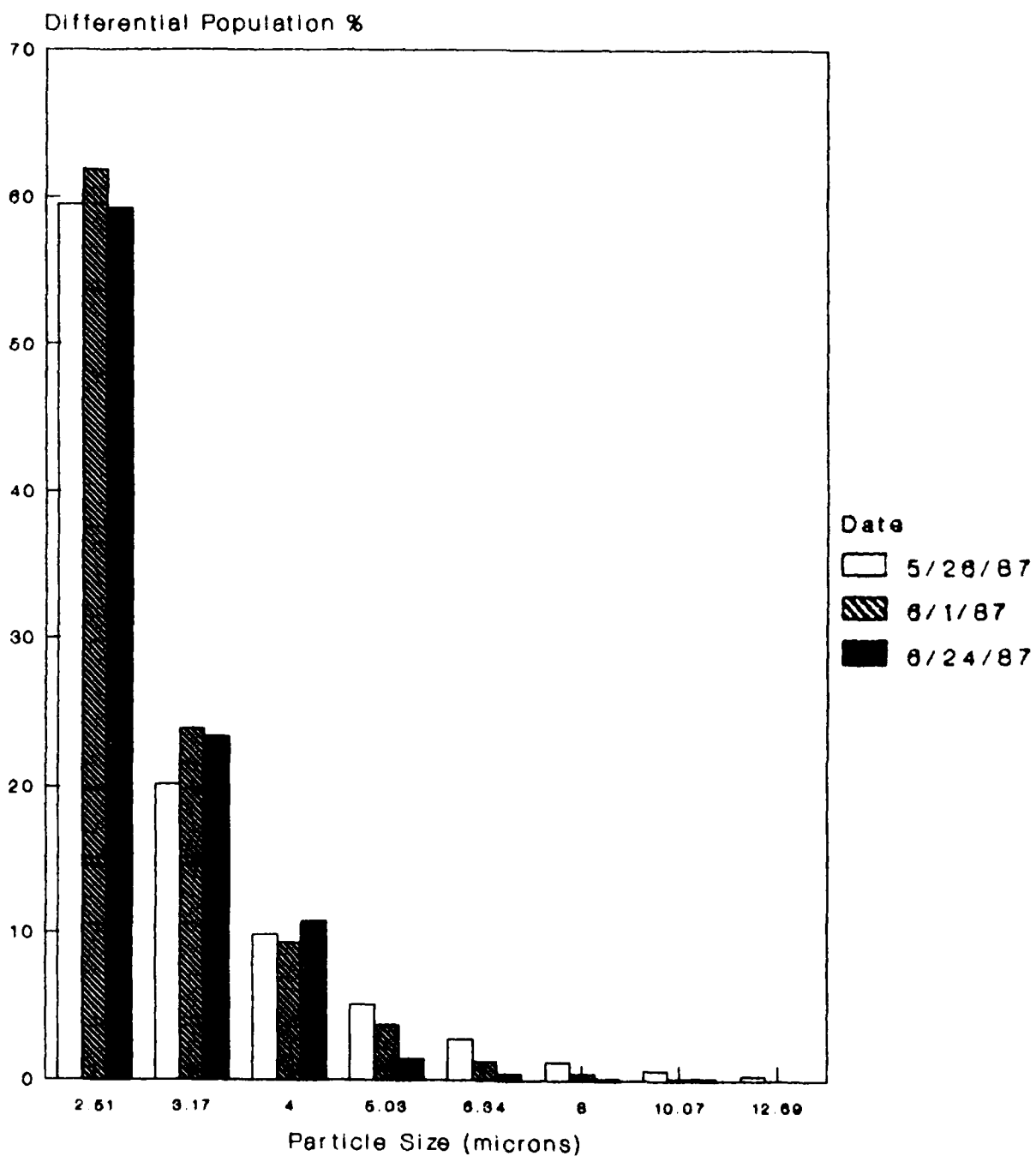
Figure 2-20.   Particle Size Distribution, XA-3995 via Coulter Counter
Method as a Function of Aging in the Tank

was first used on 5-26-87, and it still had a reasonable particle size distribution after about one month in the tank. The particle size analysis was not continued beyond this period; however, we can compare results for CEDSABP 11 versus CEDSABP 2RR in Tables 2-13 and 2-14, respectively. It is apparent that CEDSABP 2RR, which showed limited bath life, did indeed show a substantial increase in the larger particle sizes as a function of aging in comparison to CEDSABP 11. We believe that this test should be included in bath life studies of any future programs in this area.

2.3.4.2   Resin Analysis via High-Performance Liquid Chromatography -- The instrument used was a Hewlett-Packard 1084B chromatograph. THF/Water (50/50, isochratic) was the mobile phase, and the column was a Hamilton PRP-1. The detector was a UV detector operated at 254 nm. Exemplary chromatograms are shown in Figure 2-21. Various peaks appear and disappear using this analysis, and we could not resolve all of the complexities of chromatogram behavior within the program structure. An analytical technique should be fully developed for the analysis of XA-3995 in any future work.

2.3.4.3   Solvent Analysis via Gas Chromatography (GC) -- This technique was fully developed in this work because of the necessity of close monitoring of the solvent level in the primer. The instrument used was a Hewlett-Packard GC #9840, and the column was a Carbowax 20000 on Supelcoport, 80-100 mesh. The injection temperature was 225°C. The column temperature was a 40°C to 200°C gradient, and the carrier gas was helium at 30 milliliters/minute.

The technique, described in greater detail in Appendix B, was accomplished as follows: Remove a small amount of sample of XA-3995 from the tank and weigh it. Add a known amount of a standard solvent which has no interferences with the XA-3995 solvents; Hexylene glycol and toluene are possible choices. The GC instrument will provide the percent of area each peak has with respect to the total area under the peaks.

**Table 2-13. Particle Size Analysis of CEDSABP 11
As a Function of Aging on the Roller Mill**

| PARTICLE SIZE (MICRONS) | DIFFERENTIAL POPULATION PERCENT | | | | |
| | DAYS OF AGING | | | | |
	0	7	14	21	26
2	0	0	0	0	0
2.51	69.8	46.0	43.2	71.3	73.1
3.17	20.2	38.3	37.5	18.3	17.1
4	6.5	13.8	12.3	6.3	5.8
5.83	2.2	1.6	4.7	2.6	2.4
6.34	0.7	0.1	1.4	0.8	0.9
8	0.2	0	0.4	0.2	0.3
10.07	0	0	0.1	0	0.1
12.69	0	0	0	0	0

Table 2-14. Particle Size Analysis of CEDSABP 2RR
as a Function of Aging on the Roller Mill

PARTICLE SIZE (MICRONS)	DIFFERENTIAL POPULATION PERCENT DAYS OF AGING				
	0	7	14	21	28
2	0	0	0	0	0
2.51	43.5	74.9	20.1	12.6	18.1
3.17	33.3	17.1	31.9	6.8	9
4	16	5.3	19.8	3.7	4.4
5.83	5.2	1.9	12.3	2.7	2.7
6.34	1.3	0.4	8.4	4.7	4.2
8	0.3	0.1	5	16.2	15.1
10.07	0.1	0	1.7	29.1	26.1
12.69	0	0	0.3	18.8	16.6
16	0	0	0	3.8	2.9
20.15	0	0	0	0.6	0.3
25.39	0	0	0	0.2	0
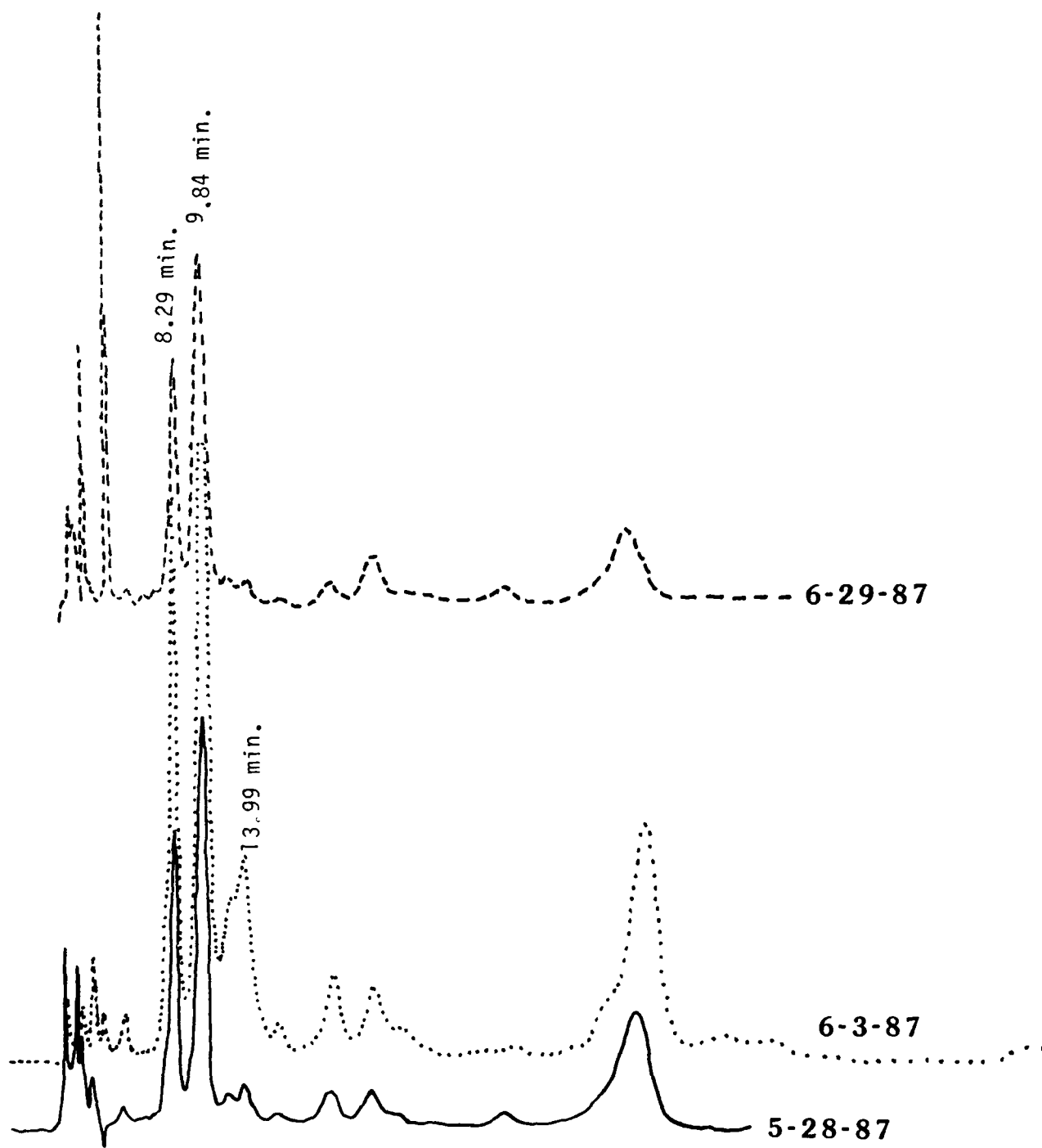
Figure 2-21. HPLC Chromatograms of XA-3995 as a Function of Aging
of the Primer in the Tank

The areas are then normalized with respect to the known amount of standard. The required solvent amounts are as follows:

Resin Solvent	1.55 weight percent
Resin Solvent 2	0.97 weight percent
Coalescing Solvent	2.66 weight percent

An exemplary output of our GC as well as an example computation is shown in Figure 2-22.

2.3.4.4   Acid Content via pH Meter -- The pH of a water dispersion is the combination of the acid and basic character of all of the soluble components in the media. There is no simpler technique for determining gross changes in the acid content of XA-3995 than pH determination. The pH was measured using an Orion Research Model 901 and a combination pH electrode. The results of these measurements will be discussed below in the paragraph concerning events in the life of the initial batch of XA-3995.

2.3.4.5   Total Ionic Content via Conductivity -- The conductivity measurements were done by means of a General Radio Model 1650B Impedance Bridge and a platinized platinum electrode with cell constant of about 0.1. The conductivity measurements were made in the electrodeposition cell using full strength XA-3995. These results are discussed in this section (2.3.4, Bath Life).

2.3.4.6   Gravimetric Component Analysis -- The objective of this analysis was to explore a way to determine the amount of each component in the XA-3995. Every particle in XA-3995 will have a different electrophoretic mobility. As XA-3995 is used up, there may be an enrichment in one component or another. As a result, it would be
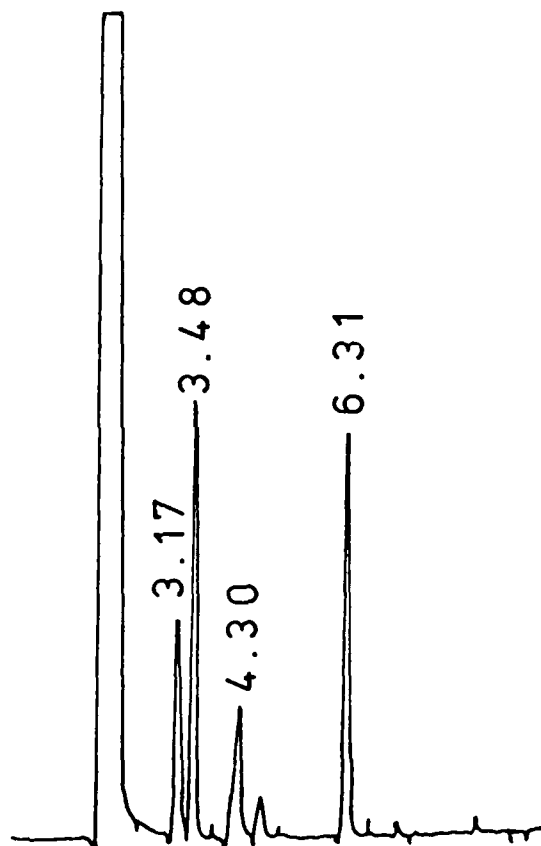
Figure 2-22.   Sample CG Output for XA-3995 at 11.35 Percent Nonvolatiles
Using Toluene as an Internal Standard

The following is the correspondence of retention times:

3.17 – resin solvent 1, 3.48 – internal standard,

4.30 – resin solvent 2, and 6.31 – coalescing solvent

advantageous to have a method by which each component could be monitored individually. The method developed is as follows:

a. Weigh sample of primer into a clean, preweighed centrifuge tube.

b. Centrifuge for 1 hour at 3000 rpm.

c. Decant and weigh supernatent.

d. Dry supernatent at 350°F until constant weight is reached.

e. Weigh centrifuge tubes to determine weight of centrifugate.

f. Dry centrifugate at 350°F until constant weight is obtained.

g. Ash centrifugate at 1000°F.

h. Cool tubes and reweigh.

An example of this method (run in duplicate) is shown in Table 2-15. The agreement with an independent measurement of solids is excellent.

2.3.4.7   Deposition Characteristics -- The deposition characteristics of the sample of XA-3995 generated in May of 1987 were monitored as described in Section 2.2.3.3. A history of this sample is presented in Section 2.3.5.

2.3.4.8   Strength of Adhesive Bonds -- The lap shear strength of adhesive bonds made with XA-3995 put into service in May of 1987 were determined as a function of the age of the primer. The lap shear tests run were Items 5 and 6 in Table 2-5, except the only test temperatures used were ambient and 325°F.

Table 2-15. Example Component Analysis Method

	SAMPLE #1	SAMPLE #2
Weight in Centrifuge Tube (g)	14.0067	14.0082
Weight of Decanted Supernatant (g)	12.8024	12.7013
Dry Weight of Supernatant (g)	0.9754	0.9633
Centrifugate Weight (g)	1.1321	1.2471
Dry Weight of Centrifugate (g)	0.3815	0.3944
Weight of Ash (g)	0.1142	0.1157
FRACTION	SAMPLE #1	SAMPLE #2
Resin in Suspension	0.9754/12.8024= 0.0762	0.9633/12.7013= 0.0758
Solids in Centrifugate	0.3815/1.1321= 0.337	0.3944/1.2471= 0.316
Pigment	0.1142/14.0067= 0.0082	0.1157/14.0082= 0.0083
Crosslinker + Adsorbed Resin	(0.3815-0.1142)/ 14.0067=0.0019	(0.3944-0.1157)/ 14.0082=0.0019
Resin Suspended in Sample	0.9754/14.0067= 0.0696	0.9633/14.0083= 0.0688
Total Solids	0.0969	0.097
Independent Measurement	0.0952	

2.3.5　　　　**HISTORY OF THE TEST SAMPLE OF XA-3995** -- The sample of
XA-3995 generated and put into service in May of 1987 was monitored for
almost a year.　The experience with this sample of XA-3995 is best
presented as a history.　The history of the sample is shown in
Table 2-16.　As seen in Table 2-16, the sample of XA-3995 was used in
3M's laboratory tank without modification until July 14, 1987.　At this
point, the solids level was becoming low, even though the performance had
not changed (both shear and deposition characteristics were fine).　The
solids level was approaching 5 percent, which the primer can easily
operate, but this point was selected as the appropriate time to attempt a
replenishment.　The replenishment was carried out as described in Section
2.3.6, and it appeared to be successful.　No obvious problems with
coating characteristics were found until August 19, 1987, when the edges
seemed to be depositing more heavily than the center.　This point was
selected to carry out dialysis of the material as described in
Section 2.3.7.　Dialysis, in general, causes reduction of the solids of
the resin; therefore, replenishment was again carried out successfully.

The pH and conductivity of XA-3995 seemed to change with use of the
material.　The expected trend is increasing pH and conductivity with use
because of the liberation of the water compatibilizing acid.　This trend
is usually followed.　There is also a tenuous correlation indicating that
a sudden drop in pH is a sign of primer destabilization.　This should be
investigated in any future studies of this material.

Strength of lap shear specimens made with adherends primed with XA-3995
were determined periodically through the time-frame of bath aging.
Figures 2-23 through 2-28 show the results of lap shear strength tests
for both aluminum and titanium adherends for up to 6 months from the
start-up of the batch.　Strength results had not changed although the
primer had been dialyzed and replenished several times.

2.3.6　　　　**REPLENISHMENT METHOD** -- The replenishment method developed in
this stage of the program is shown in Table 2-17.　The technique is based
on the use of the undiluted starting material as the replenishment
medium.　A determination is made of the solids of the XA-3995 in use, as

Table 2-16. History of Phase I, Stage II

DATE	pH	1/σ(Ω)	sq. ft	%NV
05-27-87	5.2	119		9.29
	Solvent added to prevent flaking on titanium			
06-01-87	5.21	103.5		8.35
06-05-87			11.7	
06-10-87			18.14	
06-18-87	5.1	96		
06-22-87				9.07
06-24-87	5.05	145	28	8.71
07-14-87	4.5	137	130	6.06
	Tank solids low, replenishment experiment			
07-17-87	5.14	105		9.52
07-28-87	Replaced vinyl tubing on tank with polypropylene to reduce solvent loss			
08-19-87	Panels deposit heavily on edges			
08-19-87	4.58	90		9.32
09-02-87	3.9	62	145	
	Dialysis using Spectra/Por 6 membrane			
09-04-87	3.7 - 4.5	7200		
	Now has good throwpower			
09-11-87				5.12
	Add replenishment resin			
09-11-87	5.4	115		9.15

Table 2-16. History of Phase I, Stage II (Cont.)

DATE	pH	$1/\sigma(\Omega)$	sq. ft	%NV
09-24-87	5.4	87		
	Dialyzed for 69.5 hours			
09-27-87	4.5	137		8.4
10-16-87	Dialysis			
10-19-87	4.3	252		
10-20-87	4.3	250		
10-21-87	4.4	265		
10-22-87	4.4	290		
10-23-87	4.32	325		
10-27-87	4.35	340		
10-29-87	4.45	385		
11-05-87	4.9	395		6.03
	Pump problems -			
	Lost all but 3250 ml.			
11-18-87	4.69	410		
	Replenished tank			
11-24-87	4.9	164		
	Good coatings			
12-17-87	4.67	160		
01-05-88	4.55	160	Good Coatings	
01-06-88	Some coagulant found in tank			4.95
April 88	Pump stopped, primer coagulated			
	Lactic acid added to redisperse			
	Got good panels but primer metastable			
	Work ceased			

Figure 2-23. Lap Shear Strengths as Function Priming Date
XA-3995/AF-143/PAA 2024-T81 Aluminum
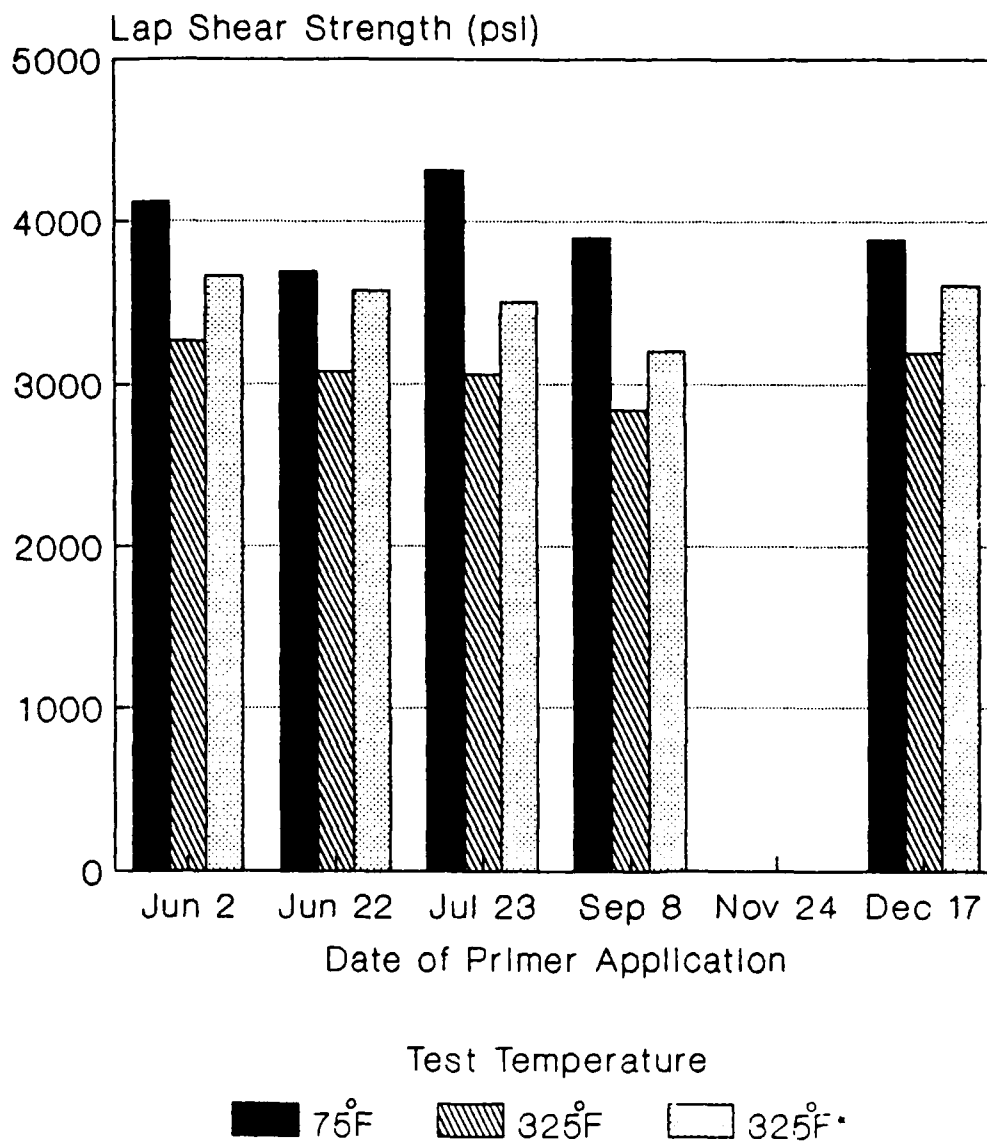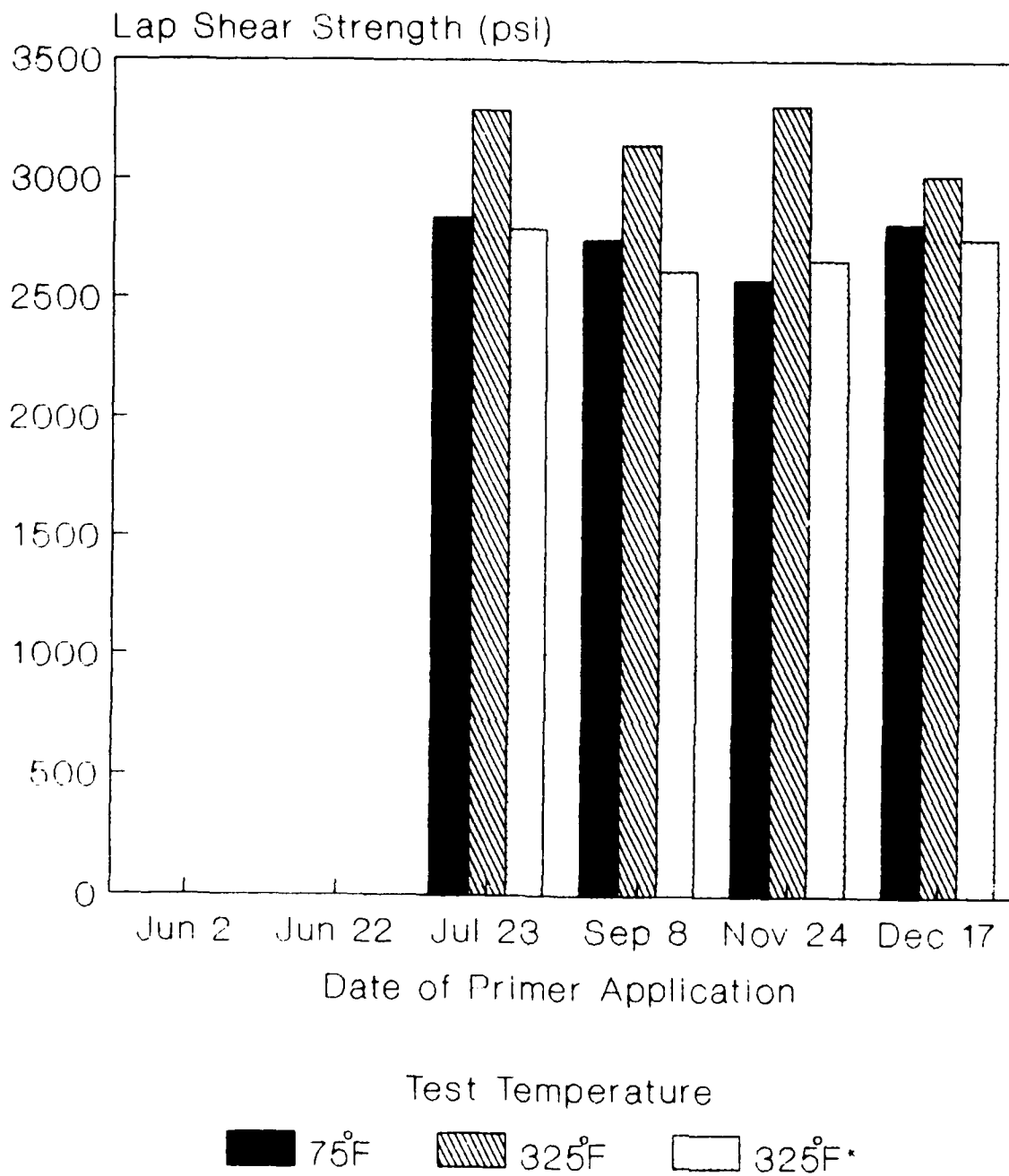
*After Exposure to 200 Hours at 350F

2-66

Figure 2-24. Lap Shear Strengths as Function Priming Date
XA-3995/AF-131-2/PAA, 2024-T81 Aluminum

Figure 2-25. Lap Shear Strengths as Function Priming Date
XA-3995/AF-131-2/PAA, 2024-T81 Aluminum

Figure 2-26. Lap Shear Strengths as Function Priming Date
XA-3995/AF-143/CrO$_3$ Ti-6A1-4V

Figure 2-27. Lap Shear Strengths as Function Priming Date
XA-3995/AF-131-2/CrO$_3$ Ti-6A1-4V

Figure 2-28.   Lap Shear Strengths as Function Priming Date
XA-3995/AF-131-2/CrO$_3$ Ti-6A1-4V

Table 2-17. Replenishment Method

1. Determine volume of remaining primer

2. Determine percent solids

3. Calculate amount of replenishment primer to add

    (a) Remaining volume (in cc) x 1.027 g/cc x percent solids = Remaining solids in grams = R

    (b) Q = Solids in original charge = Grams of Original charge x 0.1

    (c) Amount of replenishment primer to be added = (Q-R)/0.4

4. Use remaining primer to "let down" replenishment primer

5. Bring primer volume back to original volume by adding distilled water

well as its volume. A calculation is made to determine the amount of undiluted XA-3995 to be added to the XA-3995 in use. The primer in use is used to "let down" the undiluted primer. After the viscosity break is noted, the diluted primer can be added to the main tank. The percent of solids is then adjusted to approximately 10 percent by the addition of distilled water. The level of solvent in the primer must be checked after such a replenishment.

2.3.7   DIALYSIS AND REDISPERSION TECHNIQUES -- Dialysis is a technique which uses a permeable selective membrane to separate materials by their molecular weight. The membrane used was Spectra/Por 6 membrane tube which had a molecular weight cutoff of 1000. This would allow the passage of all soluble salts and acids, but would not allow the passage of the water compatible base polymer. The plumbing setup is shown in Figure 2-29. The membrane tube is placed in a tank filled with distilled water; then the tube is connected at the ends with the normal tank plumbing. Extreme care must be taken in connecting the ends of the membrane to the plumbing because of the fragile nature of the membrane. The material is allowed to circulate through the system containing the membranes until throwpower or proper coating quality has returned.

2.3.8   OTHER REGENERATION TECHNIQUES -- Early in this program, some simple experiments were performed regarding regeneration of the primer. On one sample of primer which had coagulated badly, an attempt was made to regenerate the material by the addition of base since the material had become too acidic. This did not regenerate the material, nor did the addition of solvents. We then tried to use the original acid (lactic acid) and the material did regenerate. We noted that as acid was added, the pH increased rather than decreased. This is probably due to the nature of the CEDSABP base polymer which contains several different amine functionalities, each of which has an individual pK_B. Excess shear from stirring the CEDSABP can destabilize colloids causing them to coagulate. As the colloid separates from solution, it sheds its water compatibilizing acid which decreases the pH. If more acid is added, the
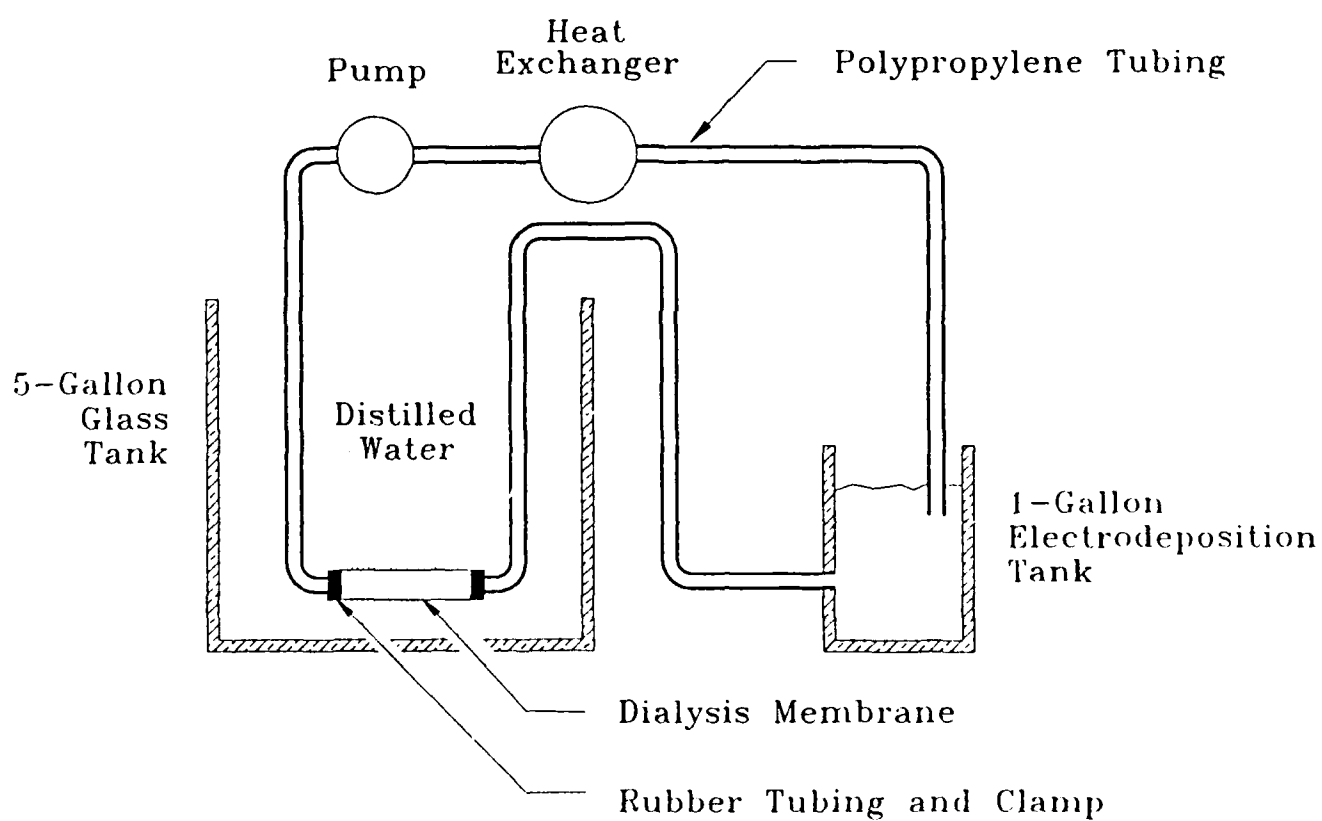
Figure 2-29. Tank Plumbing Setup

equilibrium could shift back to solubilization of the colloid and increase pH as more of the acid is associated with the base polymer. This technique should be further investigated in future programs.

2.3.9 **CURE SCHEDULE** -- Panels of XA-3995 were cured at 350°F for different lengths of time. A cure time of 45 minutes was adequate to obtain solvent resistance of the cured primer. It is recommended that the cure schedule be 1 hour at 350°F.

2.3.10 **PRIMER THICKNESS AS A FUNCTION OF APPLIED VOLTAGE AND TIME** -- Two variables were changed in this experiment: (1) The deposition time, and (2) the deposition voltage. The results of this study are shown in Tables 2-18 and 2-19 for aluminum and titanium, respectively. This experiment was repeated, with less detail, several times during the life of the tank. In general, the thickness as a function of deposition parameters changes as a function of the primer's age. Therefore, we recommend that thickness-voltage-time curves be generated periodically, perhaps daily, on the primer bath as it ages during use.

2.3.11 **CONCLUSIONS TO PHASE I, TASK I, STAGE II** -- The following are the conclusions to Phase I, Task I, Stage II:

- XA-3995 can be cured in as little as 45 minutes at 350°F, but a cure schedule of 1/2-hour air-dry and 1 hour at 350°F is recommended.

- Solids content is not important (up to a point) to coating quality.

- Solvent content and degree of solvent suspension are very important to coating quality.

- A method for solvent content determination has been developed.

Table 2-18. Cured Primer Thickness on Aluminum
(mils)

VOLTAGE (VOLTS)	APPLICATION TIME (SEC)			
	2	5	10	20
10	–	0.03	0.032	0.075
20	0.04	0.04	0.028	0.08
30	0.07	0.055	0.15	0.072
40	0.07	0.08	0.11	0.088
50	0.073	0.09	0.12	0.23
60	0.072	0.084	0.104	0.19

Table 2-19. Cured Primer Thickness on Titanium
(mils)

VOLTAGE (VOLTS)	APPLICATION TIME (SEC)			
	2	5	10	20
10	0.01	0.024	0.022	0.05
20	0.02	0.05	0.08	0.086
30	0.05	0.06	0.11	0.08
40	0.05	0.07	0.074	0.1
50	0.05	0.13	0.11	0.1
60	0.096	0.13	0.157	0.1

- Primer lifetime is presently about 3 months in our facility without rework; with rework, the primer lifetime is estimated to be in excess of 6 months.

- A mechanism of long-term primer instability is not understood but seems to be related to shear history.

- The pH and conductivity methods are not predictive of primer performance.

- Particle size measurements may be used to predict primer performance and life.

- Dialysis can prolong primer life and improve throwpower.

- Lactic acid can be added back to redisperse coagulated resin.

3/ PHASE I, TASK II
SELECTION OF WATER-BASE PRIMER MATERIALS

3.1 INTRODUCTION

In Task II of Phase I, we looked to the industry and to other likely sources for water-base materials which were potentially useful as adhesive bonding primers. Successful materials had to perform satisfactorily with qualified 350°F curing adhesive materials used in the manufacture of bonded aircraft structures. The service temperature range requirement was from -65°F to 325°F; however, the program goal, a fully serviceable 350°F adhesive/water-base primer system, would be a major achievement. Another goal, as important as meeting standard military and federal specification performance requirements, was to achieve a high degree of corrosion resistance. Preferably, this would be accomplished by formulations which did not incorporate chromates or other environmentally objectionable materials. Thus, very tangible advantages were foreseen for water-base primers by eliminating environmentally objectionable solvents and possibly objectionable corrosion resistant additives.

3.2 WATER-BASE PRIMER SCREENING

The ground rules established by the request for proposal for this contract limited the water-base primer inquiry to approximately 25 percent of the total program effort. This included Phase I, Task III screening work as well as the Phase I, Task II discovery effort. Direct research and development of a water-base primer was beyond the intent of the program; rather, a search of literature and of likely sources in the industry for existing formulations/applicable technology was the preferred approach.

The literature proved to be very sparse over the past 10 years in references on water-base primer technology. Our survey was conducted using the chemical abstracts data base with the following key search areas:

1) Water-thinned adhesive primers
2) Water-base aircraft paints
3) Water-base coatings.

A bibliography of the literature survey is given in Appendix C. We did not find any information which aided us in the procurement of a candidate water-base primer material.

Concurrently with the literature search, we canvassed the aerospace materials industry and later the industrial finishes industry for candidate water-base primer materials. The aerospace adhesives industry produced three candidate water-base materials. The candidate primer materials were as follows:

PRODUCT	SOURCE
XB-3983	3M Co.
XEA-9289	Dexter Hysol
XWBP-17GJ	American Cyanamid

Each source was a manufacturer of structural adhesive materials and familiar with the intended application and performance requirements of the primers. Preliminary data were requested from the manufacturer showing (1) capability of meeting military specification performance criteria at -65 to 325°F; (2) corrosion resistant properties; and (3) compliance with California Pollution Control requirements, before a primer was accepted into the program. Additional water-base primer materials were reported to be under development by other aerospace adhesive manufacturers but were not submitted. An inorganic base primer was potentially available to the program but required funding for further development which was not available.

A search of the paint and finishes industry did not identify any water-base primers which appeared to be serviceable at 325°F. The material nearest to program requirements was a conventional water-base zinc chromate primer. This material had been developed and qualified as a replacement for military specification grade organic solvent-base zinc chromate primer. Although the water-base zinc chromate primer was developed for use with conventional aircraft paints/finishes, it was included in the program to assess its performance as a primer for adhesive bonding. We did not expect it to meet 325°F/350°F performance criteria but thought that it might be of interest for 250°F applications, particularly for repair work. Water-base zinc chromate primers are usually stock materials where aircraft manufacturing/repair activities are performed. The water-base zinc chromate primers selected for test were as follows:

PRODUCT	SOURCE
44-GN-11	Deft Inc.
44-R-8A	Deft Inc.

Table 3-1 gives the test matrix to which the candidate primers were screened. The mechanical test specimen configurations used were metal-to-metal lap shear, wedge crack and honeycomb sandwich tested in flatwise tension and climbing drum peel. The sheet metal stock used for all test configurations was phosphoric acid anodized 2024-T81 aluminum. The honeycomb core was 5052 alloy aluminum. Candidate primer materials were applied to the phosphoric acid anodized substrates, then bonded with AF-143 adhesive and tested per the appropriate specification. A more detailed discussion of the test specimen materials, configurations, and test procedures is given in Section 4-1. The test specimen performance goals for Task II and for the program are listed in Tables 3-1 and 4-1 respectively.

Table 3-1. Phase I, Task II Test Matrix

ADHESIVE TBD 2024-T81 BARE WB PRIMERS	TEST METHOD	TEST	TEST METHOD MIN. VALUE	NO. TEST SPECIMENS
X	MMM-A-132A	LAP SHEAR, METAL TO METAL	MMM-A-132	5
X		-67°F	2750 PSI AVG	5
X		75°F	2750	5
X		270°F	2300 (FMS-1013B)	5
X		350°F	1800 (FMS-1013B)	5
X		75°F AFTER 192 HRS AT 350°F/325°F	1800 (FMS-1013B)	
	BOEING	WEDGE CRACK, 2 HRS AT 140°F, 95-100% RH CORROSION, SCRIBED PANELS	0.2" MAX.	5
X		1000 HRS AT 140°F, 95-100% RH	TBD	3
X		1000 HRS B-117 SALT FOG	TBD	3
		FILM PROPERTIES	TBD	1
X		THICKNESS/FILM QUALITY	TBD	1
X	ASTM-D-3363	FILM HARDNESS, PENCIL	TBD	1
X	FED SPEC 401	ADHESION, MANDREL - METHOD 6222	NO SEPARATION	1
X		SOLVENT RESISTANCE, 200 MEK RUB	NO REMOVAL	1
X	ASTM D-3281	IMPACT	NO FRACTURE	1
	MIL-A-25463B	SANDWICH FLATWISE TENSILE	MIL-A-25463B	5
X		-67°F	800 PSI AVG	5
X		75°F	750	5
X		270°F	465	
X		350°F/325°F	350 (FMS 1013)	
		SANDWICH PEEL CD	MIL-A-25463B	5
X		67°F	10 IN/LB	5
X		75°F	10	5
X		180°F	10	

3.2.1 SPECIMEN PREPARATION -- All of the water-base primer materials procured for Task 2 were formulated for spray application. We tried to dip-apply two of the primers, XB-3983 and XEA-9289, but failed to produce acceptable primer films. Spray equipment recommended for the application of water-base materials was used to apply the five water-base primer materials. The equipment used is described in Paragraph 4.2.2.

Each primer material required a fairly extensive trial effort before acceptable primer films were achieved. The desired primer thickness range was 0.0002-inch to 0.0004-inch based on industry standards for conventional (solvent-base) adhesive primers.

The corrosion resistant pigment component was troublesome in the XA-3983 material, approximately 80 percent of the pigment having settled within 7 minutes after agitation was stopped. We were unable to produce a XA-3983 primed panel equal in appearance to that of the manufacturer; therefore, we screened both Rohr-primed and 3M-primed panels to see what effect primer appearance had on bond strength.

3.2.2 TEST RESULTS -- Tables 3-2 through 3-7 give the results of the Task II screening tests. Table 3-2 lists the cured film properties and primer film test results for the materials screened. The XA-3983 primer tended to produce film thicknesses on the thin side of the tolerance range when applied by our technique. It was also uneven in appearance as previously mentioned. The thin primer and uneven coating produced was probably porous as evidenced by the poor salt spray performance shown in Photograph 3-1. Photographs 3-1 through 3-8 show the corrosion effects caused by exposure to 30 days ASTM-B-117 salt fog and 1000 hours (42 days) of 95 percent relative humidity at 140°F respectively. The chromate based primers XWBP-17GJ (Photograph 3-3) and 44-6N-11 (Photograph 3-4) performed well in the salt fog environment. The non-chromated XEA-9289 (Photograph 3-2) and the thinly coated (possibly porous) chromated XB-3983 (Photograph 3-1) had significant corrosion after salt-fog exposure. The XEA-9289 was not corroded to the extent of the XB-3983, probably as a result of its thicker nonporous coating. The non-chromate pigment used in XEA-3983 was obviously not as corrosion

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Table 3-2. Film Properties, Water-Base Primers

FILM PROPERTIES	PRODUCT			
	3M	HYSOL	AMERICAN CYANAMID	DEFT
	XB-3983	XEA-9289	XWBP-17GJ	44-GN-11
Texture	Semi-Gloss	Semi-Gloss	Semi-Gloss	Semi-Gloss Satin Finish
Color	Light-Yellow	Light-Yellow	Metallic Green	Light Green
Uniformity	Uniform	Uniform	Uniform	Uniform
Film Thickness (±0.3 mil)	0.17	0.35	0.33	0.2 - 0.5
Pencil Hardness	9H	9H	9H	9H
General Comments	One-Part System	One-Part System	Two-Part System	Two-Part System
Corrosion Inhibitor	Chromate	Non-Chromate	Chromate	Chromate
	(Requires frequent mixing to avoid setting of pigment)			
FILM TESTS				
200 MEK Rub	No effect	No effect	No effect	No effect
Mandrel Flexibility 180° Bend (Cone)	No cracks or separation	No cracks or separation	No cracks or separation	No cracks or separation
Impact (80 inch/lbs)	No cracks or separation	No cracks or separation	No cracks or separation	No cracks or separation
Corrosion, Scribed Panels				
Salt Fog	Heavy	Moderate	Slight	Slight
Humidity	None	None	None	None

Table 3-3. Lap Shear Test Results, Water-Base Primers (Spray Applied) on AF-143 Bonded, Phosphoric Anodized 2024-T81 Aluminum

PRIMER TYPE	TEST TEMPERATURE									
	-67°F		75°F		270°F		350°F		75°F After Exposure 192 hours @ 325°F	
	Strength (psi)	Failure Mode	Strength (psi)	Failure Mode	Strength (psi)	Failure Mode	Strength (psi)	Failure Mode	Strength (psi)	Failure Mode
3M, XB-3983	4390		4010		3280		2610		3480	
	4070	Cohesive	5580	Adhesive	3280	Cohesive	2720	Adhesive	3730	Adhesive
	4710		3890	Cohesive	3310		2560	Cohesive	3550	Cohesive
	4590		3910		3350		2600		3780	
	4420		5510		3320		2740		3330	
	X̄ 4435		X̄ 4580		X̄ 3310		X̄ 2645		X̄ 3475	
	Sx 240		Sx 882		Sx 29.5		Sx 79		Sx 184	
	% 5.5		% 19.2		% 0.9		% 3.0		% 5.2	
HYSOL, XEA-9289	3600		4200		3540		2800		3800	
	3890	Primer	3810	Primer/	3460	Cohesive	2520	Adhesive	3080	Adhesive
	4020		4080	Cohesive	3460		2610	Cohesive	3510	Cohesive
			4040		3450		2510		3280	
			4360		3630		2510		3400	
	X̄ 3840		X̄ 4100		X̄ 3510		X̄ 2590		X̄ 3415	
	Sx 215		Sx 204		Sx 77		Sx 125		Sx 268	
	% .56		% 5.0		% 2.2		% 4.8		% 7.9	
AMERICAN CYANAMID, XWBP-17GJ	3280	Primer	4090	Adhesive	2520	Adhesive	2120	Adhesive	3140	Adhesive
	3390		4070	Cohesive	2710	Cohesive	1650	Cohesive	3060	Cohesive
	3220		3720		2930		1870		3280	
	3670		3800		2820		1970		3140	
	3570		4020		2950		1970		3140	
	X̄ 3425		X̄ 3940		X̄ 2785		X̄ 1915		X̄ 3150	
	Sx 190		Sx 167		Sx 177		Sx 173		Sx 79	
	% 5.6		% 4.2		% 6.4		% 9.1		% 2.5	
DEFT-GN-44-11	2810	Adhesive	2670	Adhesive	2140		1330	Adhesive	2540	Adhesive
	3030	Cohesive	2810	Cohesive	2050		1350	Cohesive	2860	Cohesive
	3050		2680		2040		1350		2500	
	3390		2780		2070		1430		2750	
	3000		2840				1380		2780	
	X̄ 3055		X̄ 2755		X̄ 2075		X̄ 1370		X̄ 2685	
	Sx 210		Sx 77		Sx 45		Sx 39		Sx 157	
	% 6.9		% 2.8		% 2.2		% 2.8		% 5.9	

NOTE: Lap shear bonds were fabricated with AF-143 Supported Adhesive (0.06 lb/ft^2)

Data rounded to ± 5

Table 3-4. Lap Shear Test Results - Miscellaneous Water-Base Primers (Spray Applied) on AF-143 Bonded, Phosphoric Acid Anodized 2024-T81 Aluminum

TEST TEMPERATUE	PRIMER TYPE					
	3M, XB 3983 (PRIMED BY 3M)		DEFT-44-GN-11		DEFT-44-R-8A	
	STRENGTH (psi)	FAILURE MODE	STRENGTH (psi)	FAILURE MODE	STRENGTH (psi)	FAILURE MODE
75°F	3890 4029 3960 3960 3960 $\bar{x}$ 3960 S_x 47 % 1.2	Primer/ Cohesive	3790 4090 4080 4040 4050 $\bar{x}$ 4010 S_x 124 % 3.1	Adhesive/ Cohesive	2000 1970 2140 2040 2000 $\bar{x}$ 2030 S_x 66 % 3.3	Cohesive
350°F	2470 2540 2550 2100 2690 $\bar{x}$ 2470 S_x 224 % 9.1	Cohesive	2090 2070 2080 1830 2330 $\bar{x}$ 2080 S_x 177 % 8.5	Primer/ Cohesive	1110 1010 1010 984 966 $\bar{x}$ 1020 S_x 57 % 5.7	Adhesive

NOTE: Lap Shear Bonds were fabricated with AF-143 Supported Adhesive (0.06 lb/ft^2)
Data rounded to ±5

Table 3-5. Sandwich Flatwise Tensile (FWT) Test Results, Water-Base Primers (Spray Applied) on AF-143 Bonded, Phosphoric Acid Anodized 2024-T81 Aluminum

TEST TEMPERATURES

PRIMER TYPE	-67°F FWT Strength in lb/in	-67°F Failure Mode	75°F FWT Strength in lb/in	75°F Failure Mode	270°F FWT Strength in lb/in	270°F Failure Mode	325°F FWT Strength in lb/in	325°F Failure Mode
3M, XB-3983	1410 1380 1370 1460 1490 x̄ 1420 Sx 53 % 3.8	Cohesive	1020 1040 1100 1010 1050 x̄ 1045 Sx 35 % 3.4	Cohesive	654 628 582 625 606 x̄ 619 Sx 27 % 4.4	Cohesive	499 550 494 545 498 x̄ 517 Sx 28 % 5.4	Cohesive
Hysol, XEA-9289	1310 1300 1350 1440 1320 x̄ 1345 Sx 57 % 4.2	Cohesive	992 1000 945 1020 998 x̄ 991 Sx 28 % 2.8	Cohesive	582 607 541 614 580 x̄ 585 Sx 29 % 4.9	Cohesive	467 487 475 464 480 x̄ 475 Sx 9 % 2.0	Cohesive
Am. Cyanamid, XWBP-17GJ	1090 1330 1350 1220 1380 x̄ 1275 Sx 119 % 9.4	Cohesive	1010 990 864 971 1030 x̄ 973 Sx 65 % 6.7	Adhesive/ Cohesive	624 662 608 675 635 x̄ 641 Sx 27 % 4.3	Adhesive/ Cohesive	473 412 473 524 417 x̄ 460 Sx 46 % 10	Adhesive/ Cohesive
DEFT-44-GN-11	1180 1050 1170 1250 1170 x̄ 1165 Sx 72.0 % 6.2	Adhesive/ Cohesive	986 930 997 979 999 x̄ 978 Sx 28 % 2.9	Adhesive/ Cohesive	502 530 487 561 525 x̄ 521 Sx 28 % 5.4	Adhesive/ Cohesive	331 320 293 311 317 x̄ 314 Sx 14.0 % 4.5	Adhesive/ Cohesive

NOTE: 2024-T81 Bare Al; 5052 Al Honeycomb Core (1/4" cell size)
Data rounded to ±5

Table 3-6. Sandwich Climbing Drum Peel Test Results, Water-Base Primers (Spray Applied) on AF-143 Bonded, Phosphoric Acid Anodized 2024-T81 Aluminum

| PRIMER TYPE | T E S T   T E M P E R A T U R E S | | | | | |
| | -67°F | | 75°F | | 180°F | |
	Peel Strength in lb/in	Failure Mode	Peel Strength in lb/in	Failure Mode	Peel Strength in lb/in	Failure Mode
3M, XB-3983	21.5	Adhesive/	12.1	Adhesive/	11.6	Adhesive/
	19.1	Cohesive	14.6	Cohesive	12.6	Cohesive
	21.5		13.1		11.6	
	19.5		14.1		11.6	
	19.0		13.6		11.6	
	X̄ 20.1		X̄ 13.5		X̄ 11.8	
	Sx 1.3		Sx 1.0		Sx 0.4	
	% 6.3		% 7.1		% 3.8	
Hysol, XEA-9289	24.6	Adhesive/	14.6	Adhesive/	13.7	
	25.1	Cohesive	14.2	Cohesive	13.2	Adhesive/
	22.1		15.6		13.1	
	22.6		15.1		11.7	
	20.1		17.6		14.2	
	X̄ 22.9		X̄ 15.4		X̄ 13.2	
	Sx 2.0		Sx 1.3		Sx 0.9	
	% 8.8		% 8.6		% 7.1	
American Cyanamid, XWBP-17GJ	16.7	Primer/	13.3	Cohesive	6.7	Adhesive/
	22.2	Adhesive/	12.5		9.2	Cohesive
	20.2	Cohesive	12.9		8.7	
	20.7		13.3		8.7	
	28.2		13.3		8.7	
	X̄ 21.6		X̄ 13.0		X̄ 8.4	
	Sx 4.2		Sx 0.3		Sx 1.0	
	% 19.4		% 2.6		% 11.6	
DEFT-GN-44-11	24.3	Adhesive/	26.0	Adhesive To Core	19.1	Adhesive To Core
	25.9	Cohesive	25.6		19.2	
	25.6		25.3		18.9	
	21.3		26.0		19.0	
	24.0		26.1		19.8	
	X̄ 24.2		X̄ 25.8		X̄ 19.2	
	Sx 1.8		Sx 0.3		Sx 0.4	
	% 7.5		% 1.3		% 1.8	

NOTES: 2024-T81 Bare Al; 5052 Al Honeycomb Cure (1/4" cell size)
Data Rounded to ± 5

Table 3-7. Wedge Crack Propagation Test Results, Water-Base Primers (Spray Applied) on AF-143 Bonded, Phosphoric Acid Anodized 2024-T81 Aluminum

PRIMER TYPE	WEDGE CRACK PROPAGATION (INCHES) AFTER 24 HOURS AT 140°F/95-100% RH	
3M, XB-3983	0.020	0.025
	0.010	0.050
	0.020	
	$\bar{X}$ 0.025	
	Sx 0.015	
	% 60.0	
Hysol, XEA-9289	0.045	
	0.005	0.030
	0.030	0.025
	$\bar{X}$ 0.027	
	Sx 0.014	
	% 53.3	
American Cyanamid, XWBP-17GJ	0.137	0.162
	0.190	0.166
	0.182	
	$\bar{X}$ 0.167	
	Sx 0.02	
	% 12.3	
DEFT-44-GN-11	0.040	0.065
	0.057	0.107
	0.041	
	$\bar{X}$ 0.062	
	Sx 0.027	
	% 44.0	

Photograph 3-1. 3M, XB-3983 Primed 2024-T81 Aluminum, 1000 Hours Exposure to ASTM B-117 Salt Fog

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Photograph 3-2. Hysol, XEA-9289 Primed 2024-T81 Aluminum, 1000 Hours
Exposure to ASTM B-117 Salt Fog
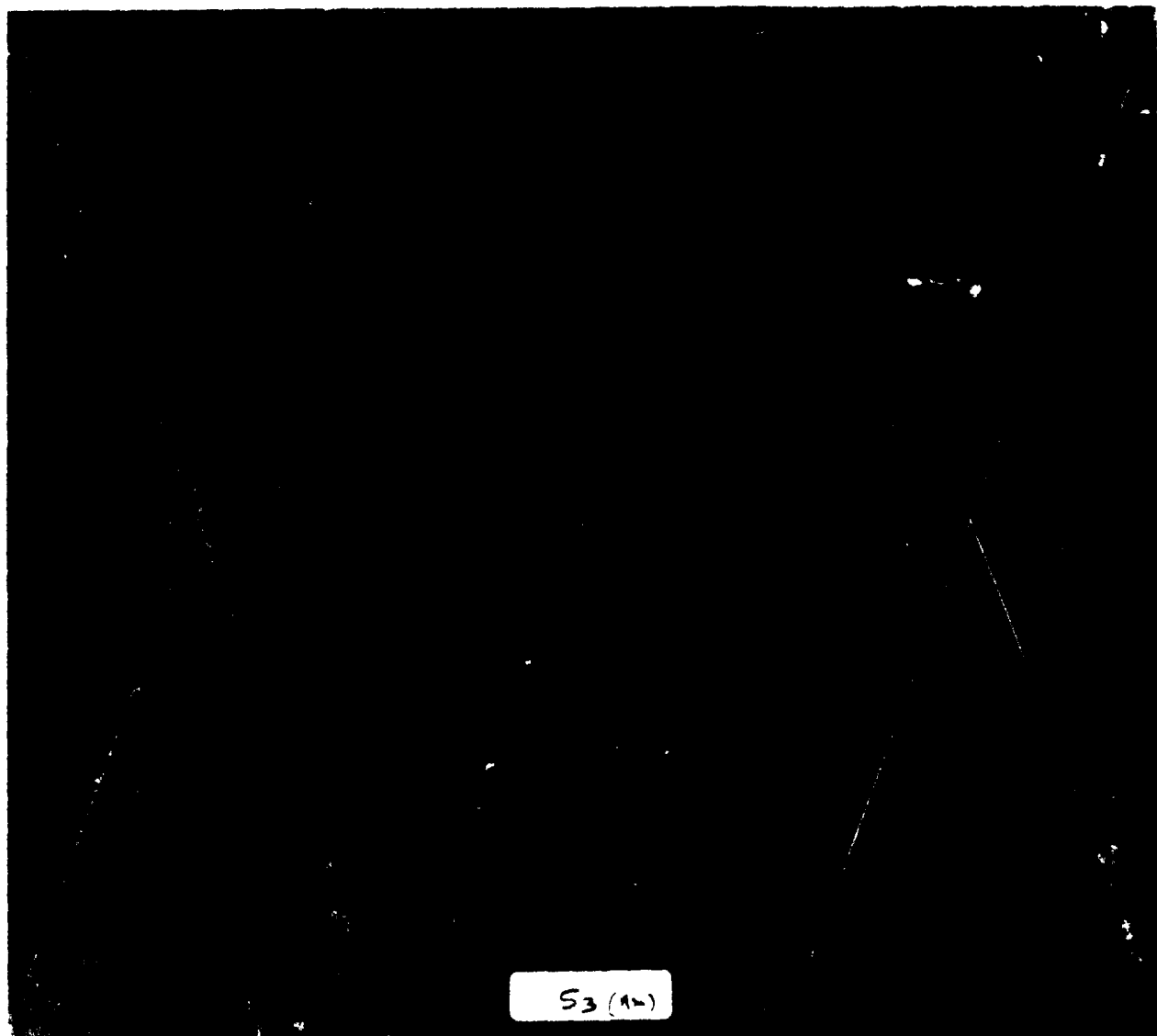
Photograph 3-3. American Cyanamid, XWBP-17GJ Primed 2024-T81 Aluminum, 1000 Hours Exposure to ASTM B-117 Salt Fog

$S_1 (D)$
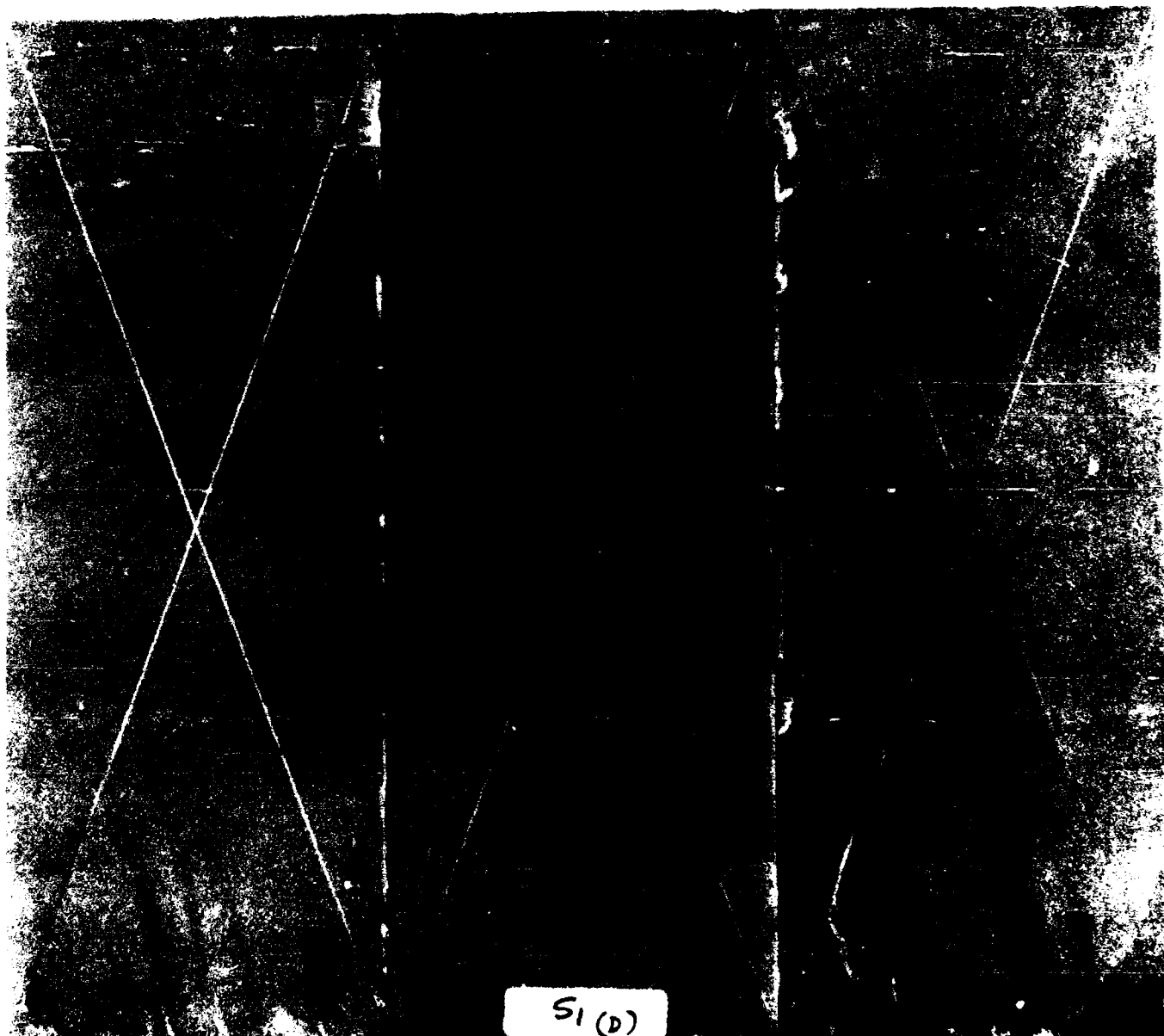
Photograph 3-4. Deft-44-GN-11 Primed 2024-T81 Aluminum, 1000 Hours
Exposure to ASTM B-117 Salt Fog
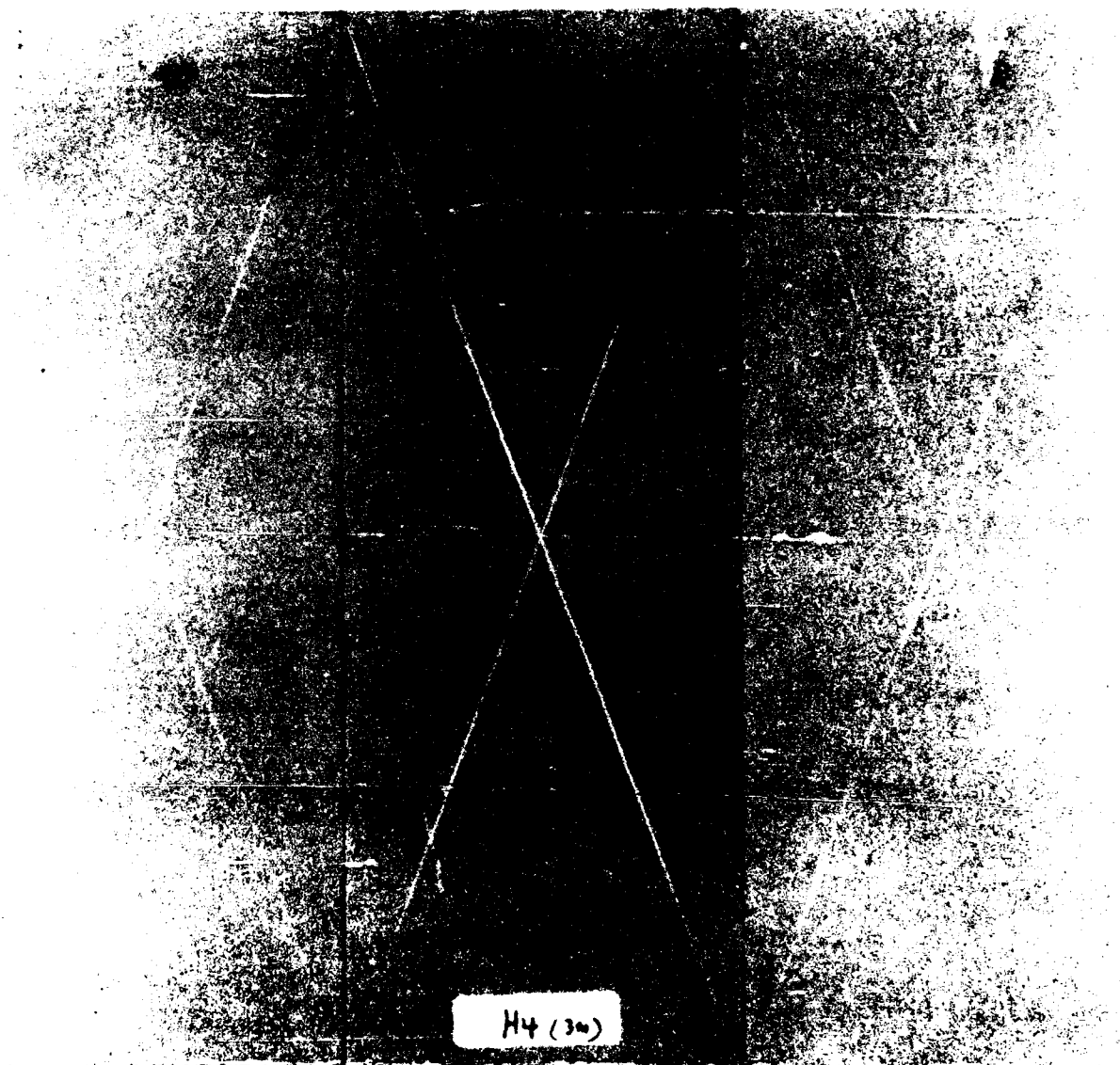
Photograph 3-5. 3M, XB-3983 Primed 2024-T81 Aluminum, 1000 Hours
Exposure at 140°F, 95-100% RH

H_L (H)
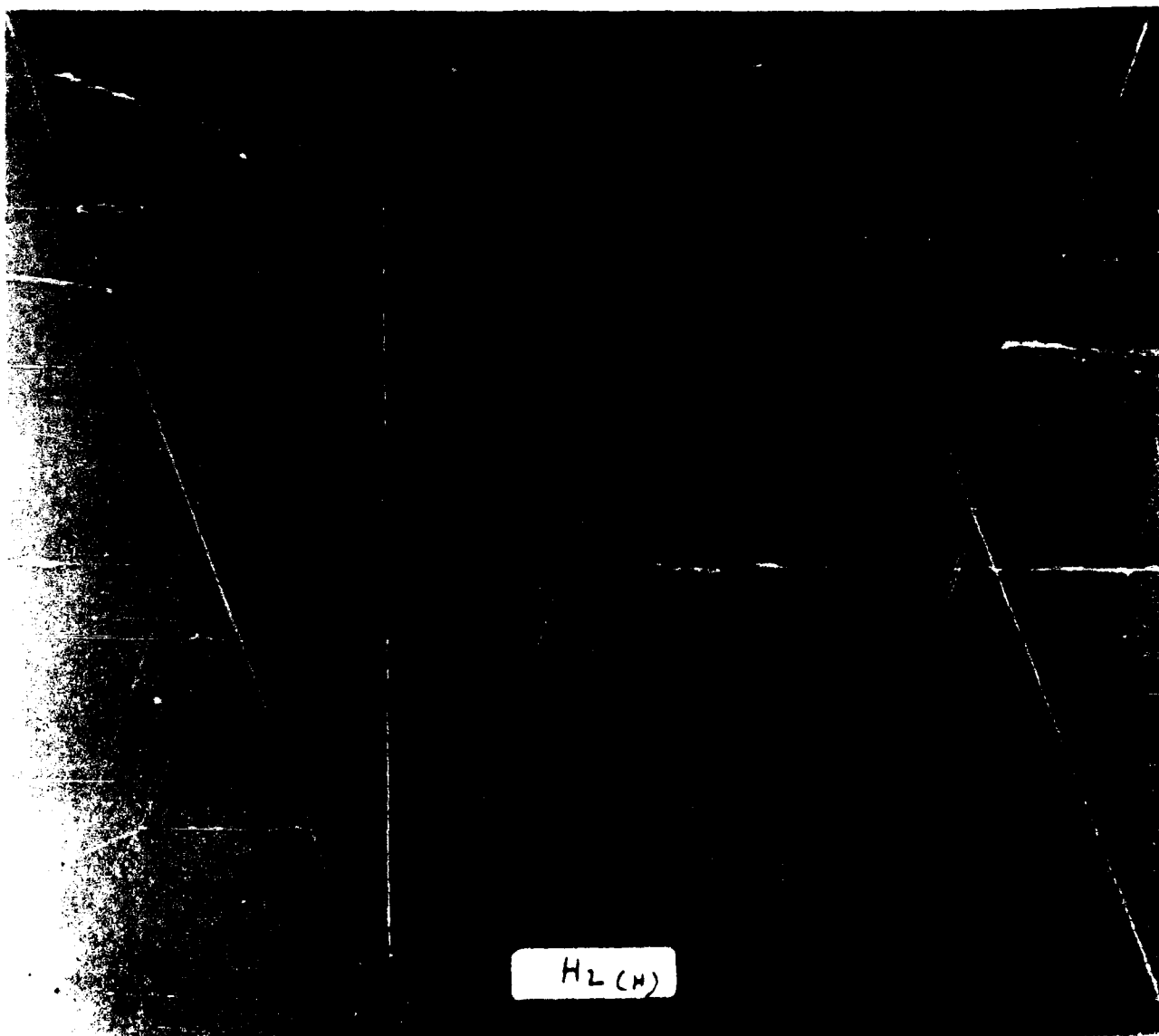
Photograph 3-6. Hysol, XEA-9289 Primed 2024-T81 Aluminum, 1000 Hours
Exposure at 140°F, 95-100% RH

Photograph 3-7. American Cyanamid, XWBP-17GJ Primed 2024-T81 Aluminum, 1000 Hours Exposure at 140°F, 95-100% RH
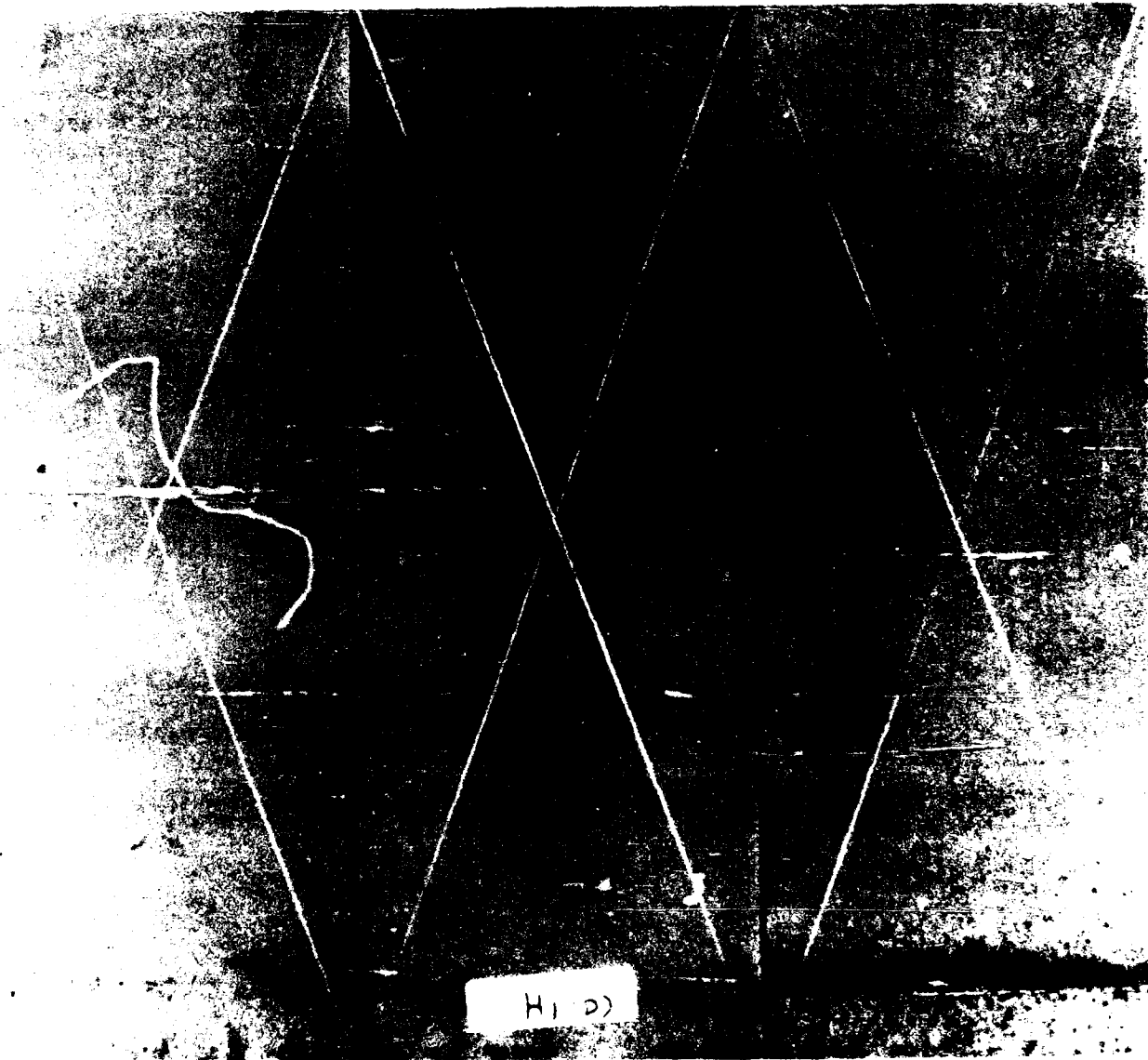
Photograph 3-8. Deft-44-GN-11 Primed 2024-T81 Aluminum, 1000 Hours
Exposure at 140°F, 95-100% RH

resistant as the chromate pigments used in the other primers. All of the primers (Photographs 3-5 through 3-8) performed well in humidity exposure.

Mechanical bond strength test results (Tables 3-3 through 3-7) all exceed military and federal specification requirements established for the program (Table 4-1) with a few minor exceptions. These exceptions are as follows:

1) Deft-44-GN-11 failed to achieve the program goals (Table 3-1) of 2300 psi and 1800 psi lap shear strength at 270°F and 350°F respectively in one set of tests but exceeded the 350°F requirement in another; however, we did not expect a water-base zinc chromate paint primer to perform this well at 350°F.

2) Deft-44-R-8A (Table 3-4) failed to meet both the 75°F and the 350°F lap shear strength program goals (Table 3-1) and was withdrawn from further testing.

3) Only Deft-44-GN-11 failed to meet the 325/350°F flatwise tensile strength requirement.

4) American Cyanamid XWBP-17GJ failed to achieve the 10 lb/inch peel strength requirement (Table 3-1) at 180°F.

3.2.3   PRIMER SELECTION FOR PHASE I, TASK III SCREENING -- All of the water-base primer systems, which were carried completely through Task II testing, demonstrated sufficient capability to be considered as candidates for Phase I, Task III screening. A simple ranking procedure was used to select a primer for Task III screening. The results of the rankings are shown in Table 3-8. In the ranking exercise, each primer is listed in the order in which it finished for each test condition. The lower the total of the primer numerical ranking, the higher the probability of its success in Task III.

Table 3-8. Ranking of Primers in Order of Placement
for Each Test Condition

PROPERTY	XB-3983	XEA-9289	XWBP-17GJ	44-GN-11
FLEXIBILITY	1	1	1	1
ADHESION (IMPACT)	1	1	1	1
CORROSION				
SALT SPRAY	4	3	1	1
HUMIDITY	1	1	1	1
LAP SHEAR				
-67°F	1	2	3	4
75°F	1	2	3	4
350°F	1	2	3	4
AGING	1	2	3	4
SANDWICH FWT				
-67°F	1	2	3	4
75°F	1	2	4	3
270°F	1	3	2	4
325°F	1	2	3	4
SANDWICH PEEL CD				
-67°F	4	2	3	1
75°F	3	2	4	1
180°F	3	2	4	1
WEDGE CRACK	1	2	4	3
TOTAL	26	31	43	41

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The sum of the rankings shows that XB-3983 is slightly ahead of XEA-9289 and that 44-GN-11 is slightly ahead of XWBP-17GJ. There is a significant gap between the rankings of the first and second place primers and the third and fourth place primers. Therefore, the third and fourth place primers were not further considered. Also, 44-GN-11 demonstrated only marginal capability for 325/350°F service. This was a program requirement and could not be further considered without additional testing.

XEA-9289 was selected over XB-3983 for Task III screening even though the latter scored a little higher in the overall ranking. The principle concern with XB-3983 was the poor corrosion resistance this primer system displayed and the difficulty we had in spraying it. We suspect that the poor corrosion resistance of XB-3983 may have been due to poor coating quality.

3.3   CONCLUSIONS

Water-base primers have been available to the industry since the late 1960s. They have not been used extensively, primarily because of the difficulty of producing uniform coatings and for some materials the inconvenience of using a catalyzed system which had a limited pot life. Original water-base primers were significantly overshadowed by the solvent-base systems with regard to film properties and ease of use. Another reservation to the use of water-base primers at that time was the dissimilarity of the primer resin with that of the adhesive. It has generally been the practice within the industry to make the primer from the same resin/curing agent materials as the adhesive, to avoid any question of the compatibility between the adhesive and the primer. This may be an issue with little merit, since the industry has bonded successfully to organic resin matrix composites for many years. Still, the question of incompatibility may arise when the makeup and application of the primer is not within the control of the adhesive manufacturer. The adhesive manufacturers usually disclaim their product in such cases, insisting that they provide both the primer and the adhesive material.

The water-base primer materials tested in Phase I, Task II of the program represent a significant improvement over a water-base primer we tested in 1968. Most notable was the significant improvement in film uniformity. The earlier product tended to run excessively and leave irregular deposits of chromate corrosion resistant pigment which resulted in a variable primer thickness/uniformity.

The thickness of the primer film can influence adhesive bond strength, especially if the application is too thick. This is a significant factor affecting bond strength, especially for the more rigid/brittle primers. If the primer film is too thin, corrosion resistance may suffer as a result of voids or thin spots in the coating. How thick or thin the primer is applied becomes both a matter of technique/equipment and the characteristics of the primer. These interrelationships are amplified further in Paragraph 4.2. New techniques, skills and suitable equipment were required which varied for each of the primers tested. The development of application techniques was outside the program scope. The XEA-9289 material responded best to our efforts, while the XB-3983 proved more difficult to work with. Ease of application was therefore a major factor in selecting XEA-9289 for Task III screening.

All of the primers tested, except the paint primers (Deft), demonstrated the capability for meeting military specification requirements for both metal-to-metal and sandwich bond strength. With further refinement of the primer formulation(s) and application technique(s), water-base primers could rival current solvent-base primer materials.

Finally, we were quite surprised at how well one of the paint primer formulations performed as an adhesive primer. Although the performance at 350°F was marginal, we estimate that it would be serviceable at 250°F and possibly as high as 300°F. The corrosion resistance of this material was outstanding compared to the other primers tested, which is not surprising, considering that it was specifically formulated for corrosion resistance.

4/ PHASE I, TASK III
SCREENING OF ELECTRODEPOSITED AND WATER-BASE PRIMER MATERIALS

4.1   INTRODUCTION

Task III of Phase I began the task of assessing the ability of the electrodeposited primer and the spray deposited water-base primer selected in Phase I, Tasks I and II to meet the objectives of the program. The main objectives of the program were to provide a primer material qualified for -65°F to 325°F service for fabricating adhesive bonded structure for military aircraft. In turn, the main objective was supplemented by several specific objectives which the primer must meet in order to achieve a "qualified" status. A summary of military specification requirements for qualification is given in Table 4-1. In Task III, the progressive process scale-up with an increasing test base was initiated. This was continued throughout the program. The objective was to demonstrate a level of basic adhesive system performance, within a definable process envelope, for a successful primer material.

4.1.1   SCREENING TEST RATIONALE -- Initially, the plan was that the screening test procedures would utilize fundamental military and federal test specimen configurations and quantities as required for qualifying adhesive materials. Likewise, trial priming of test specimens was performed in quantity, providing both statistical assessment of performance and real-time processing experience to determine the acceptance of the primer as a production-feasible material. This scale-up, production readiness/qualification philosophy is typical of industry-wide practices where sufficient data is available to indicate

Table 4-1. Summary of Military Specification Requirements

TEST CONDITION	TEST METHOD / MIN. VALUE
Lap Shear, Metal/Metal	MMM-A-132A
10 min @ -67°F	2750 psi avg
75°F	2750
270°F	2300 (FMS-1013)
350°F/325°F	1800 (FMS-1013)
Lap Shear, Laminate/Aluminum	FMS-1013
10 min @ -67°F	1350 psi avg
75°F	1600
270°F	1100
350°F/325°F	1050
Lap Shear @ 75°F After	MMM-A-132A
7 days in MIL-T-5624 JP-4	2750 psi avg
7 days in MIL-H-83282 fluid	2750
30 days @ 120°F, 96-100% RH	2750
30 days ASTM B-117 salt fog	2750
192 hours @ 350°F/325°F	1800 (FMS-1013)
10^6 cycles fatigue	750
Lap Shear Creep Rupture	MMM-A-132A
192 hours @ 1600 psi/RT	0.015" max
192 hours @ 800 psi/350°F/325°F	0.015"
300 hours @ 2000 psi/RT	0.015"
300 hours @ 1700 psi/270°F	0.015"
10 hours @ 1200 psi/350°F/325°F	0.015"
Lap Shear, Stress Durability, Cyclic	Douglas
1500 psi cyclic @ 160°F, 95-100% RH	TBD
Lap Shear, Stress Durability Sustained	Douglas
1200 psi 90 days @ 160°F, 95-100% RH	No Failure
Wedge Crack	Boeing
2 hours @ 140°F, 95-100% RH	0.2" max

TEST CONDITION	TEST METHOD / MIN. VALUE
Corrosion, Scribed Panels	
1000 hours @ 140°F, 95-100% RH	TBD
1000 hours ASTM B-117 salt fog	TBD
Instrumental Analysis	3M
SEM, AES, SIMS, ESCA, etc.	
Film Deposition	3M
Time/volts/thickness	TBD
Thickness/film quality	TBD
Film hardness, pencil	ASTM-D-3363 / No separation
Adhesion, MIL-STD-401-Method 6222	No removal
MEK resistance, 200 Rub	
Impact, ASTM D-3281	TBD
Bath Analysis	3M
Soluble/non-soluble solids	TBD
Volatile/non-volatile content	TBD
Conductivity	TBD
PH, temperature	TBD
Sandwich Flatwise Tensile	MIL-A-25463B
10 min @ -67°F	800 psi avg
75°F	750
180°F	465
270°F (FMS-1013)	
350°F/325°F (FMS-1013)	350
Sandwich Short Beam Shear	MIL-A-25463
10 min @ -67°F	625 psi avg
75°F	610
350°F/325°F (FMS-1013)	435
350°F/325°F after 192 hrs @ 350°F	350/315

TEST CONDITION	TEST METHOD / MIN. VALUE
Short Beam Shear @ 75°F after	MIL-A-25463B
30 days @ 120°F, 95-100% RH	1800/1350 lbs
30 days MIL-T-5624, JP-4	1800/1350 lbs
Sandwich Short Beam Creep	MIL-A-25463
192 hours @ 75°F, 1000 lb load	0.025" max
192 hours @ 350°F 1000 lb load	0.050" max
Sandwich Long Beam Shear	FMS-1013B
10 min @ -67°F	2275 lb avg
75°F	225
270°F	600
350°F/325°F	625
400°F	475
Sandwich Long Beam Creep	FMS-1013B
300 hours @ 270°F, 150 psi stress	0.090" max
20 hours @ 350°F/325°F, 115 psi stress	0.180" max
Sandwich Peel, Climb Drum	MIL-A-25463B
20 min @ -67°F	10 in lb
75°F	10
180°F	10
Metal/Metal T-Peel	MMM-A-132A
75°F	10 lb/in *
-67°F	10 lb/in *
Lap Shear, Metal to Metal	FMS-1013
350°F/325°F, 300 hrs @ 300°F, 10 hrs @ 350°F	1800 psi avg
Flatwise Tensile	FMS-1013B
350°F/325°F, 300 hrs @ 300°F 10 hrs @ 350°F	668 psi avg

* No Reqm't - Program Goal

that a material is a candidate for the intended end use. Both the electrodeposited and the water-base primer materials demonstrated sufficient performance characteristics to be considered for -65°F to 325°F use. The first level of scale-up testing was conducted to determine potential for continuing through the remainder of the scale-up/qualification program.

4.1.2   TEST SPECIMEN ADHEREND AND ADHESIVE MATERIALS SELECTION -- Task III of Phase I screening considers the bondline performance of the primer when used with two different adhesive materials on phosphoric acid anodized 2024-T81 and 7075-T6 aluminum alloys and chromic acid anodized 6Al-4V titanium alloy. The T81 condition was achieved by aging 2024-T3 at 375°F for 12 hours (MIL-A-8705). The phosphoric acid anodize surface preparation (SAE, ARP-1524) was specified by the contract, and chromic acid anodize (MIL-A-8625) surface preparation was selected for titanium. Several adhesive materials were used during the program. AF-143 was used for Phase I, Task I of the program in order to correlate the current primer development task (Task I) with previous work performed under Air Force Materials Laboratory Contract F33615-80-C-5069. Phase I, Task II selection of water-base primers also used AF-143 adhesive to correlate with Task I electrodeposited primer optimization work. Beginning with Phase I, Task III, the water-base primer and electrodeposited primer evaluation, AF-131 and RB-398 adhesive materials were selected for the program on the basis of their qualified status for use on the F-111 aircraft. The primer materials would have to perform satisfactorily with both of these adhesives in order to be considered as candidates to qualify for F-111 use. A third adhesive, AF-131-2 (an asbestos-free version of AF-131), was used later in the program when it became apparent that a closer comparison was required between 3M and Rohr test results. The Air Force Project Engineer concurred with the use of AF-131-2, since AF-131 was being phased out because of its asbestos content; AF-131 was scheduled for replacement by AF-131-2 when it achieved qualified status.

4.1.3   HONEYCOMB CORE MATERIAL SELECTION -- Honeycomb core material selected for the Phase I, Task III of the program was 5052 aluminum with 1/4-inch cell size, 7.9 pounds/cubic foot which corresponds to

MIL-A-25463 requirements. Normal MIL-A-25463 sandwich requirements (shear, flatwise tensile) were specified in the military specifications requirements summary with extrapolated values for 270°F and 350°F based on FMS-1013 requirements. FMS-1013 requirements are based on 1/8-inch cell core which is approximately double in bond area compared to 1/4-inch cell MIL-A-25463 core, and test values passing MIL-A-25463 are expected to meet FMS-1013 values which are not proportionally greater. Full compliance to MMM-A-132 and MIL-A-25463 was required and incorporated as part of the this contract.

4.1.4   TASK III, SCREENING TEST SELECTION -- Selected Military (MIL-A-25463) and Federal (MMM-A-132) test specimen configurations were used for Task III screening which determined basic metal-to-metal lap shear and sandwich flatwise tension and shear properties of bonded specimens made with both water-base and electrodeposited primer materials. The basic test configurations were selected to be repeated as appropriate for each new task/scale-up level throughout the remainder of the program. With each new task screening, additional MIL-A-25463/MMM-A-132 test configurations/environments were to be added to the basic test specimen configuration complement so that by the end of the program, complete qualification to all requirements of MIL-A-25463/MMM-A-132 would have been completed. For Task III screening, honeycomb climbing drum peel and metal-to-metal peel were the specification requirements added for screening the influence of primer toughness in the bondline. There were, however, no MMM-A-132 nor FMS-1013 "T" peel requirements. A 10-pounds/inch requirement was established for comparison purposes. Corrosion resistance was screened in Task III by a 30-day exposure of lap shear specimens to ASTM B-117 salt fog prior to testing. Task III also screened stressed bondline durability and interfacial bond integrity through combined lap shear stress (sustained loading) and the 2-hour wedge-crack extension test exposure at 90-100 percent relative humidity at 140°F. Specimens were failed at the completion of the stress exposure period and examined as appropriate using optical microscopy and scanning electron microscopy complemented with energy dispersive spectrometry. The 3M Company was to furnish additional instrumental examination service

using XP5, AES, and other instrumentation as appropriate for the final examination prior to recommending that the program proceed to Phase II. This work was not undertaken because of unresolved thickness and porosity problems with the electrodeposited primer. The Phase I, Task III test matrix is shown in Table 4-2.

4.2 WATER-BASE PRIMER

Phase I, Task III application and screening of the XEA-9289 water-base primer selected out of Phase I, Task II were to be performed to determine a possible backup to the electrodeposited primer system. The Air Force Materials Laboratory had previously decided that the electrodeposited primer had the greatest potential for achieving superior corrosion resistance through a more uniform and complete coverage of metal airframe components. A further advantage of electrodeposited primers over the water-base primers was envisioned as cost savings through the elimination of wasteful overspray and the significant amount of labor involved in hand-spray application. Therefore, the level of effort in Task III focused on determining the adhesive bond strength performance afforded by a water-base primer system in its current state of development. No other process studies were planned for Task III beyond following the manufacturer's instructions and guidance for applying the primer to a recommended thickness. Additional analysis and process improvement would have been undertaken had water-base primer received more consideration for Phase II scale-up and qualification.

4.2.1 PRIMER APPLICATION -- Structural adhesive primers, as used in the aircraft industry since the inception of adhesive bonding, are most often applied by hand spraying. This application method, then, is well established. In spray application, the dispersed primer liquid (spray) must solidify rapidly on the surface of the substrate to be immobilized and built upon without flowing away. This is usually achieved by rapid evaporation of the liquid vehicle (solvent) portion of the primer. To date, the primer vehicle has been composed of organic solvent(s) which can be adjusted to evaporate quickly or over a wide range of conditions. Uniform coatings of precise thickness are readily attainable with organic solvent-base primers applied by conventional spray technique.

Table 4-2. Phase I, Task III Test Matrix

TEST METHOD	Test Condition	2024-T81 BARE — ADHESIVE A (EDP)	ADHESIVE A (WBP)	ADHESIVE B (EDP)	ADHESIVE B (WBP)	7075-T6 BARE — ADHESIVE A (EDP)	ADHESIVE A (WBP)	ADHESIVE B (EDP)	ADHESIVE B (WBP)	6-AL-4V TITANIUM — ADHESIVE A (EDP)	ADHESIVE A (WBP)	ADHESIVE B (EDP)	ADHESIVE B (WBP)	TEST	TOTAL
MMM-A-132A	LAP SHEAR METAL TO METAL														
	-67°F	--	X	X	X	--	X	X	X	--	X	--	X	5	45
	75°F	XC	X	X	X	XC	X	X	X	X	X	X	X	5	60
	350°F/325°F	XC	X	X	X	XC	X	X	X	X	X	X	X	5	60
	75°F AFTER 30 DAYS ASTM B-117 SALT FOG	--	X	X	X	--	X	X	X					5	30
	350°F/325°F AFTER 300 HRS 270°F, 10 HRS 350°F	X	X	X	X	X	X	X	X	X		X		3	60
	T-PEEL														
	75°F	--	X	X	X	--	X	X	X	--	X	X	X	5	45
	67°F	--	X	X	X	--	X	X	X	--	X	X	X	5	45
BOEING DOUGLAS	WEDGE CRACK, 2 HRS 140°F, 95-100% RH	X	X	X	X	X	X	X	X	X	X	X	X	5	60
	LAP SHEAR STRESS DURABILITY, SUSTAINED LOAD 160°F, 95-100% RH, 1200 PSI 90 DAYS	X	X	X	X	X	X	X	X	X	X	X	X	3	36
MIL-A-25463B	SANDWICH FLATWISE TENSILE														
	-67°F	--	X	X	X	--	X	X	X					5	30
	75°F	--	X	X	X	--	X	X	X					5	30
	350°F/325°F	XC	X	X	X	XC	X	X	X					5	40
	350°F/325°F AFTER 300 HRS, 270°F, 10 HRS 350°F	--	X	X	X	--	X	X	X					3	18
	SANDWICH SHORT BEAM SHEAR														
	350°F/325°F AFTER 192 HRS AT 350°F	XC	X	X	X									5	20
	SANDWICH PEEL, CD														
	-67°F	--	X	X	X	--	X	X	X					5	30
	75°F	XC	X	X	X	XC	X	X	X					5	40
	180°F	--	X	X	X	--	X	X	X					5	30

WBP - WATER-BASE PRIMER
EDP - ELECTRODEPOSITED PRIMER

The same mechanics of application apply to the deposition of water-base primers as to the deposition of organic solvent-base primers. There is, however, a significant difference in both the evaporation rate of the water-base primer and in its degree of compensation compared to organic solvent-base primers. Water-base primers, therefore, can be more difficult to apply evenly with uniform thickness. There is less latitude for application. New skills, equipment and techniques, which differ from those required for conventional organic solvent-base primers, are necessary; essentially, a new application art/technique had to be developed.

Rohr experienced considerable difficulty initially in the spray application of the water-base primer. Through persistent effort and guidance from the manufacturer of the primer, we progressively improved our technique to the point that satisfactory primer coatings were produced. There was, however, a "scrap rate" involved; specimens sometimes had to be remade due to faulty technique or changes in the primer material, the latter of which was usually due to increased viscosity (aging) that changed the application parameters. Settling-out of corrosion resistant pigment was also a factor.

4.2.2 SPECIMEN PREPARATION -- Water-base primer was spray-applied to phosphoric acid anodized 2024-T81, 7075-T6 aluminum and chromic acid anodized 6A1-4V Titanium and 5052 aluminum honeycomb core (1/4-inch cell). The primer thickness tolerance was 0.0002- to 0.0004-inch cured film thickness.

Test specimens of a particular type/geometry were taped to a large area substrate (usually cardboard) and spray primed as a single large area surface. The spray equipment used was a Model 62 Binks spray gun fitted with a #66S air cap and a #66 fluid tip/needle. The spray gun was operated at 50 psi. After priming, the panels were air dried for 1 hour followed by an oven cure at 350°F for 1 hour. Cured primer thickness was

verified by spot checking with an isoscope. The primer spray procedure had previously been adjusted so that for a given pressure setting, a certain number of passes with the spray gun at a set time/motion and distance from the panels would deposit a primer film within the required thickness tolerance. This procedure is normally followed in production priming practices.

Primed test panels were laid up and bonded with AF-131 and RB-398 adhesives for test configurations shown in Table 4-2. Both adhesives were cured in the laboratory autoclave at 350°F for 1 hour under 35 psi maintained throughout the cure cycle and during cool to 180°F.

4.2.3   SCREENING TESTS -- The specimens were tested at the required temperature per the appropriate military and federal specification. The strength requirements for these tests are given in Table 4-1. The results of the tests are given in Tables 4-3 through 4-14. Table 4-15 is a tabulation of the averaged lap shear data in Tables 4-3 through 4-14 which are below MMM-A-132, MIL-A-24563 and FMS-1013 requirements.

4.2.3.1   AF-131 Bonded Specimens -- The AF-131 adhesive bonds accounted for approximately 25 percent more below specification values than bonds made with RB-398 adhesive. AF-131, a relatively brittle adhesive, did not meet minimum specification values at -67°F nor at 75°F for lap shear strength. Primer to substrate failures were noted in the lap shear specimens. Primer failures were seen previously at these test temperatures in Task II specimens; however, failing stresses were much higher and all test values exceeded specification requirements. One difference between the two tests was the use of AF-143 in Task II.

After 30 days of salt spray exposure, AF-131 bonds appeared to recover, readily passing 75°F lap shear requirements. AF-131 also passed elevated temperatures lap shear and sandwich flatwise tensile strength requirements, developing the highest shear strengths obtained during the program for the AF-131/XEA-9289 combination.

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Table 4-3. Lap Shear Strength Using AF-131 Adhesive on Phosphoric Acid Anodized/XEA-9289 (Water-Base) Primed 2024-T81 and 7075-T6 Aluminum

Test Temperature	METAL ADHERENDS				
	2024-T81 Strength (PSI)		Failure Mode	7075-T6 Strength (PSI)		Failure Mode
-67°F	2340	2390	Primer	2590	2700	Primer
	2380	2480		2240	2490	
	2410	2640		2300	2520	
	x̄	2440		x̄	2475	
	Sx	109		Sx	175	
	%	4.4		%	7.0	
75°F	2270	1930	Pri/	2280	2110	Primer
	2020		Adh/	2250	2200	
	2010			2090	2280	
	x̄	2060	Coh.	x̄	2205	
	Sx	147		Sx	84	
	%	7.2		%	3.8	
350°F	3570	3510		3040	2520	
	3690	3630		3090	2770	Adh/
	3650		Coh.	3100	2570	Coh.
	3560					
	x̄	3600		x̄	2850	
	Sx	67		Sx	265	
	%	1.0		%	9.3	
350°F after 270°F, 100 hours; 350°F, 10 hours	2880	x̄ 2840	Pri/ Adh/ Coh.	2390	x̄ 2500	Pri/ Adh/ Coh.
	2930	Sx 115		2550	Sx 93	
	2710	% 4.1		2550	% 3.7	
75°F after 30 day Salt Exposure	3290	3280	Pri/ Adh	2900	2770	Pri/ Adh
	3560	3600		3290	3000	
	3180	3380		3000	3280	
	x̄	3380		x̄	3040	
	Sx	167		Sx	207	
	%	4.9		%	6.8	

NOTE: Data rounded to ±5 PSI

Table 4-4. Lap Shear Strength Using RB-398 Adhesive on Phosphoric Acid Anodized/XEA-9289 (Water-Base) Primed 2024-T81 and 7075-T6 Aluminum

Test Temperature	METAL ADHERENDS				
	2024-T81 Strength (PSI)		Failure Mode	7075-T6 Strength (PSI)		Failure Mode
-67°F	3380	3490	Primer	3930	3090	Primer
	3480	3300		3660	3070	
	3760	3280		3380	3130	
	$\bar{x}$ 3450			$\bar{x}$ 3375		
	Sx 176			Sx 353		
	% 5.1			% 10.5		
75°F	3850	3530	Primer	3960	3450	Primer
	3700	3570		3230	3640	
	3510	3830		2360	3330	
	$\bar{x}$ 3665			$\bar{x}$ 3495		
	Sx 151			Sx 267		
	% 4.1			% 7.6		
350°F	2950	2790	Pri/ Adh/ Coh.	3440	3520	Adh./ Coh.
	2840	2730		3430	3560	
	2840	2800		3410	3600	
	$\bar{x}$ 2825			$\bar{x}$ 3495		
	Sx 74			Sx 78		
	% 2.6			% 2.2		
350°F after 270°F, 100 hours; 350°F, 10 hours	3740	$\bar{x}$ 3770	Pri/ Adh/ Coh.	3610	$\bar{x}$ 3590	Pri/ Adh/ Coh.
	3750	Sx 44		3640	Sx 63	
	3820	% 1.2		3520	% 1.8	
75°F after 30 day Salt Exposure	3760	3850	Pri/ Adh	4260	3660	Pri/ Adh
	4020	3750		3630	3320	
	4050	3750		3410	3920	
	$\bar{x}$ 3865			$\bar{x}$ 3700		
	Sx 139			Sx 346		
	% 3.6			% 9.3		

NOTE: Data rounded to ±5 PSI

Table 4-5. Lap Shear Strength Using AF-131 and RB-398 Adhesives on Chromic Acid Anodized/XEA-9289 (Water-Base) Primed 6Al-4V Titanium

Test Temperature	METAL ADHERENDS				
	AF-131 Strength (PSI)		Failure Mode	RB-398 Strength (PSI)		Failure Mode
-67°F	1520 2410 1450 1700 1420 1280		Pri/ Coh	1700 1870 2460 2290 2070 1980		Primer
	$\bar{x}$ 1630 Sx 407 % 24.9			$\bar{x}$ 2060 Sx 277 % 13.5		
75°F	1390 1570 1370 1450 1520 1410		Primer	2230 2260 1840 2270 2070 2260		Primer
	$\bar{x}$ 1450 Sx 78 % 5.4			$\bar{x}$ 2155 Sx 172 % 8.0		
350°F	2950 3280 3040 3310 3110		Pri/ Coh.	1900 2270 1980 2310 2070 2420		Pri/ Coh.
	$\bar{x}$ 3140 Sx 154 % 4.9			$\bar{x}$ 2160 Sx 205 % 9.5		
350°F after 270°F, 100 hours; 350°F, 10 hours	2980 2920 2770		Pri/ Adh/ Coh.	2480 2460 2250		Pri/ Adh
	$\bar{x}$ 2890 Sx 108 % 3.7			$\bar{x}$ 2460 Sx 127 % 5.3		

NOTE: Data rounded to ±5 PSI

Boeing CAA-5V surface treatment

Table 4-6. Sandwich Flatwise Tensile Strength (1/4-Inch Cell Core) Using AF-131 Adhesive on Phosphoric Acid Anodized/ XEA-9289 Primed 2024-T81 and 7075-T6 Aluminum

| Test Temperature | METAL ADHERENDS | | | | |
	2024-T81 Strength (PSI)		Failure Mode	7075-T6 Strength (PSI)		Failure Mode
-67°F	962	1060		971	965	
	931	955	Coh.	1090	1070	Adh/
	1030	825		1080	932	Coh.
	$\bar{x}$	960		$\bar{x}$	1020	
	Sx	82		Sx	70	
	%	8.6		%	6.8	
75°F	810	922		835	969	
	928	842	Adh/	1100	983	Adh/
	1580	1010	Coh.	901	1090	Coh.
	$\bar{x}$	1015		$\bar{x}$	980	
	Sx	285		Sx	104	
	%	28		%	10.6	
350°F	569	799		797	866	
	748	577	Coh.	894	773	Coh.
	683	683		768	779	
	$\bar{x}$	677		$\bar{x}$	813	
	Sx	91		Sx	54	
	%	13.5		%	6.6	
350°F after 270°F, 100 hours; 350°F, 10 hours	574 730 740		Coh.	885 742 821		Coh.
	$\bar{x}$	681		$\bar{x}$	816	
	Sx	93		Sx	72	
	%	13.7		%	8.8	

NOTE: Data rounded to ±5 PSI

Table 4-7. Sandwich Flatwise Tensile Strength (1/4-Inch Cell Core) Using RB-398 Adhesive on Phosphoric Acid Anodized/XEA-9289 (Water-Base) Primed 2024-T81 and 7075-T6 Aluminum

Test Temperature	METAL ADHERENDS				
	2024-T81 Strength (PSI)		Failure Mode	7075-T6 Strength (PSI)		Failure Mode
-67°F	1290 1270 1220	1000 1170 1240	Adh/ Coh.	1160 1210 1360	1230 1190 1180	Adh/ Coh.
	x̄ 1200 Sx 106 % 8.8			x̄ 1225 Sx 72 % 5.9		
75°F	1120 1020 1160	1040 903 1140	Adh/ Coh.	925 1040 1020	1080 1200 947	Adh/ Coh.
	x̄ 1065 Sx 97 % 9.1			x̄ 1035 Sx 99 % 9.6		
350°F	622 554 502	625 557 586	Adh/ Coh.	535 561 516	589 536 560	Adh/ Coh.
	x̄ 575 Sx 45 % 7.8			x̄ 550 Sx 26 % 4.8		
350°F after 270°F, 100 hours; 350°F, 10 hours	628 671 745		Adh/ Coh.	673 652 603		Coh.
	x̄ 681 Sx 59 % 8.7			x̄ 643 Sx 36 % 5.6		

NOTE: Data rounded to ±5 PSI

Table 4-8. T-Peel Strength Using AF-131 and RB-398 Adhesives on Phosphoric Acid Anodized/XEA-9289 (Water-Base) Primed 2024-T81 and 7075-T6 Aluminum

AF-131 ADHESIVE

Test Temperature	METAL ADHERENDS				
	2024-T81 Strength (PSI)		Failure Mode	7075-T6 Strength (PSI)		Failure Mode
-67°F	2.0 2.0		Adh/ Coh.	3.4 2.9		Adh/ Coh.
	3.6 2.0			3.4 2.4		
	3.5 3.0			4.4 2.9		
	$\bar{x}$ 2.7			$\bar{x}$ 3.2		
	Sx .8			Sx .7		
	% 28.9			% 21.1		
75°F	1.6 1.9		Adh/ Coh.	0.9 1.6		Adh/ Coh.
	1.9 1.7			1.7 1.8		
	1.2			1.4 2.9		
	$\bar{x}$ 1.7			$\bar{x}$ 1.7		
	Sx .3			Sx .7		
	% 17.4			% 38.5		

RB-398 ADHESIVE

Test Temperature	METAL ADHERENDS				
-67°F	4.9 8.9		Adh/ Coh.	3.4 6.8		Adh/ Coh.
	6.5 6.5			3.4 4.4		
	5.0 5.0			5.8 5.4		
	$\bar{x}$ 6.1			$\bar{x}$ 4.9		
	Sx 1.6			Sx 1.4		
	% 25.3			% 28.2		
75°F	6.1 5.8		Adh/ Coh.	4.3 3.3		Adh/ Coh.
	5.8			4.8 3.1		
	5.4			5.6 3.8		
	$\bar{x}$ 5.8			$\bar{x}$ 4.2		
	Sx .3			Sx 1.0		
	% 5.0			% 22.8		

Table 4-9.   T-Peel Strength Using AF-131 and RB-398 Adhesives on Chromic Acid Anodized/XEA-9289 (Water-Base) Primed 6Al-4V Titanium

AF-131 ADHESIVE

Test Temperature	Strength lb/in		Failure Mode
-67°F	1.0	1.0	Adh/Pri.
	1.0	1.0	
	1.0	1.0	
	$\bar{x}$ = 1.0		
	Sx = 0		
	% = 0		
75°F	2.6	1.5	Adh/Pri.
	2.4	1.4	
	1.5	1.3	
	$\bar{x}$	1.8	
	Sx	.6	
	%	31.6	

RB-398 ADHESIVE

Test Temperature	Strength lb/in		Failure Mode
-67°F	2.0	1.9	Adh/Pri.
	2.4	2.4	
	2.4	2.4	
	$\bar{x}$	2.3	
	Sx	.2	
	%	10.4	
75°F	4.9	3.4	Adh/Pri.
	5.3	3.4	
	3.4	3.0	
	$\bar{x}$	3.9	
	Sx	1.0	
	%	24.4	

Table 4-10. Sandwich Short Beam Shear Strength Using AF-131 and RB-398 Adhesives on Phosphoric Acid Anodized/XEA-9289 (Water-Base) Primed 2024-T81 Aluminum

TEST TEMPERATURE 350°F AFTER 192 HOURS AT 350°F					
Adhesive	350°F				Failure Mode
AF-131	493	512	$\bar{x}$	499	Core Shear
	491	502	Sx	7.8	
	494	499	%	1.6	
RB-398	473	479	$\bar{x}$	470	Core Shear
	471	470	Sx	6.6	
	459	467	%	1.4	

NOTE: Data rounded to ±5 PSI

Table 4-11. Sandwich Climbing Drum Peel Strength Using AF-131 Adhesive on Phosphoric Acid Anodized/XEA-9289 (Water-Base) Primed 2024-T81 and 7075-T6 Aluminum

Test Temperature	METAL ADHERENDS				
	2024-T81 Strength (PSI)		Failure Mode	7075-T6 Strength lb/in		Failure Mode
-67°F	12.9	10.9		12.8	12.4	
	12.9	13.9	Adh/	9.9	12.9	Adh/
	10.5	11.9	Coh.	10.9	12.5	Coh.
	$\bar{x}$	12.2		$\bar{x}$	11.9	
	Sx	1.3		Sx	1.2	
	%	10.7		%	10.2	
75°F	8.5	10.9		9.9	9.4	
	7.7	8.5	Pri/	11.4	9.4	Adh/
	8.0	11.1	Adh/ Coh.	9.4	9.4	Coh.
	$\bar{x}$	9.1		$\bar{x}$	9.8	
	Sx	1.5		Sx	.8	
	%	16.4		%	8.2	
180°F	10.0	8.5		10.9	10.9	
	9.5	10.5	Pri/	11.7	8.9	Adh/
	8.0	9.0	Adh/ Coh.	12.2	9.9	Coh.
	$\bar{x}$	9.3		$\bar{x}$	10.8	
	Sx	.9		Sx	1.2	
	%	10.1		%	11.2	

Table 4-12. Sandwich Climbing Drum Peel Strength Using RB-398 Adhesive on Phosphoric Acid Anodized/XEA-9289 (Water-Base) Primed 2024-T81 and 7075-T6 Aluminum

Test Temperature	METAL ADHERENDS				
	2024-T81 Strength (PSI)		Failure Mode	7075-T6 Strength lb/in		Failure Mode
-67°F	13.5 14.9 17.0 16.9 19.4	Adh/ Coh.	7.9 7.4 8.4 15.3 10.4 9.4	Pri/ Adh.
	x̄ 16.3 Sx 2.3 % 13.8		x̄ 9.8 Sx 2.9 % 29.6	
75°F	19.5 17.1 17.0 14.5 20.9	Pri/ Adh/ Coh.	8.9 20.4 8.4 17.3 18.8 18.8	Pri/ Adh/ Coh.
	x̄ 17.8 Sx 2.5 % 13.9		x̄ 15.4 Sx 5.3 % 34.6	
180°F	24.0 18.0 23.4 17.0	Pri/ Adh/ Coh.	15.3 17.8 18.8 15.3 18.3 15.9	Pri/ Adh.
	x̄ 20.6 Sx 3.6 % 17.5		x̄ 16.9 Sx 1.6 % 9.4	

Table 4-13. Wedge Crack Propagation Test Results, Using AF-131 Adhesive on Phosphoric Acid Anodized/XEA-9289 Primed 2024-T81 and 7075-T6 Aluminum; and Chromic Acid Anodized (Boeing)/ XEA-9289 (Water-Base) Primed 6Al-4V Titanium Adherends

ADHEREND	INITIAL CRACK, INCHES	TOTAL CRACK LENGTH, INCHES, AFTER 2 HOURS AT 140°F/95-100% R.H.	CHANGE IN CRACK LENGTH, INCHES
2024-T81	3.86	3.97	0.11
	4.25	*	0.00
	3.04	*	0.00
	3.22	3.28	0.06
	4.08	*	0.00
			$\bar{x}$ 0.034
			Sx 0.050
			% 146.5
7075-T6	3.02	3.05	0.03
	3.92	*	0.00
	2.81	*	0.00
	3.48	3.53	0.05
	2.88	*	*
			$\bar{x}$ 0.016
			Sx 0.023
			% 143.9
6Al-4V Titanium	4.69	DEBONDED	----
	5.56	DEBONDED	----
	4.32	4.63	0.31
	INSERTION FAILURE		
	INSERTION FAILURE		

* No Change

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Table 4-14. Wedge Crack Propagation Test Results, Using RB-398 Adhesive on Phosphoric Acid Anodized/XEA-9289 Primed 2024-T81 and 7075-T6 Aluminum; and Chromic Acid Anodized (Boeing)/ XEA-9289 Primed 6A1-4V Titanium Adherends

ADHEREND	INITIAL CRACK, INCHES	CRACK LENGTH, INCHES AFTER 2 HOURS AT 140°F/95-100% R.H.	CRACK LENGTH, INCHES	
2024-T81	2.99	3.05	0.06	
	2.96	*	0.00	
	2.97	*	0.00	
	2.53	*	0.00	
	2.76	2.86	0.10	
			x̄	0.032
			Sx	0.046
			%	143.9
7075-T6	2.56	2.62	0.06	
	3.21	*	0.00	
	3.05	*	0.00	
	2.45	2.53	0.08	
	2.63	2.74	0.11	
			x̄	0.050
			Sx	0.049
			%	98.0
6A1-4V Titanium	2.88	3.03	0.15	
	2.89	3.09	0.20	
	3.05	3.45	0.40	
	3.34	3.56	0.22	
	2.43	2.83	0.40	
			x̄	0.274
			Sx	0.1173
			%	43.0

* No Change

Table 4-15. Reconciliation of Tables 4-3 through 4-14 with MMM-A-132, MIL-A-25463 and FMS-1013 Requirements   (Page 1 of 2)

ADHEREND	ADHESIVE	TEST TEMPERATURE	TEST STRENGTH PSI		REQUIREMENT PSI
2024-T81	AF-131	-67°F	2440	L/S (P)	2750 L/S (1)
7075-T6	AF-131	-67°F	1475	L/S (P)	2750 L/S (1)
Ti-6A1-4V	AF-131	-67°F	1630	L/S (P)	2750 L/S (1)
Ti-6A1-4V	RB-398	-67°F	2060	L/S (P)	2750 L/S (1)
2024-T81	AF-131	-67°F	960	FWT	1075 FWT (3)
7075-T6	AF-131	-67°F	1020	FWT	1075 FWT (3)
2024-T81	AF-131	-67°F	2.7	TP LB/IN	10 LB/IN (4)
7075-T6	AF-131	-67°F	3.2	TP LB/IN	10 LB/IN (4)
2024-T81	RB-398	-67°F	6.1	TP LB/IN	10 LB/IN (4)
7075-T6	RB-398	-67°F	3.9	TP LB/IN	10 LB/IN (4)
Ti-6A1-4V	AF-131	-67°F	1.0	TP (P)	10 LB/IN (4)
Ti-6A1-4V	RB-398	-67°F	2.3	TP (P)	10 LB/IN (4)
7075-T6	RB-398	-67°F	9.8	CDP (P)	10 LB/IN (2)
2024-T81	AF-131	75°F	2060	L/S (P)	2750 L/S (1)
7075-T6	AF-131	75°F	2205	L/S (P)	2750 L/S (1)
Ti-6A1-4V	AF-131	75°F	1450	L/S (P)	2750 L/S (1)
Ti-6A1-4V	RB-398	75°F	2155	L/S (P)	2750 L/S (1)
2024-T81	AF-131	75°F	1015	FWT	1106 FWT (3)
7075-T6	AF-131	75°F	980	FWT	1106 FWT (3)
2024-T81	RB-398	75°F	1065	FWT	1106 FWT (3)
7075-T6	RB-398	75°F	1035	FWT	1106 FWT (3)
2024-T81	AF-131	75°F	1.66	TP	20 LB/IN (4)

ADHEREND	ADHESIVE	TEST TEMPERATURE	TEST STRENGTH PSI	REQUIREMENT PSI
2075-T6	AF-131	75°F	1.70 TP	20 LB/IN (4)
2024-T81	RB-398	75°F	5.8 TP	10 LB/IN (4)
7075-T6	RB-398	75°F	4.2 TP	10 LB/IN (4)
Ti-6A1-4V	AF-131	75°F	1.8 TP (P)	10 LB/IN (4)
Ti-6A1-4V	RB-398	75°F	3.9 TP (P)	10 LB/IN (4)
2024-T81	AF-131	75°F	9.1 CDP	10 LB/IN (2)
7075-T6	AF-131	75°F	9.8 CDP	10 LB/IN (2)
Ti-6A1-4V	AF-131	75°F	0.31 WC (AP)	0.2 IN (4)
Ti-6A1-4V	RB-398	75°F	0.27 WC (AP)	0.2 IN (4)
2024-T81	AF-131	180°F	9.3 CDP	10 LB/IN (2)
2024-T81	RB-398	350°F	575 FWT	668 FWT (3)
7075-T6	RB-398	350°F	550 FWT	668 FWT (3)
7075-T6	RB-398	350°F (10 HRS)	643 FWT	668 FWT (3)

(1)   MMM-A-132
(2)   MIL-A-25460
(3)   FMS-1013
(4)   PROGRAM GOAL, NO SPECIFICATION REQUIREMENT

L/S = LAP SHEAR
FWT = FLATWISE TENSILE
TP   = "T" PEEL
CDP = CLIMBING DRUM PEEL
WC   = WEDGE CRACK
(P) = PRIMER FAILURE
(AP) = ADHESIVE/PRIMER FAILURE

4.2.3.2   RB-398 Bonded Specimens -- RB-398 passed -67°F, 75°F and 350°F lap shear and sandwich flatwise tensile strength requirements. Both AF-131 and RB-398 were a little short of achieving 10-pound/inch sandwich climbing drum peel strengths (AF-131 at 75°F and 180°F and RB-398 at -67°F). In the metal-to-metal "T" peel test, neither AF-131 nor RB-398 bond strengths approached the program goal (not a military specification requirement) of 10-pounds/inch peel at -67°F and 75°F. There was a noticeable difference in peel strength between AF-131 and RB-398 bonds, with RB-398 producing the better peel values.

Both AF-131 and RB-398 bonds to primed chromic acid anodize 6Al-4V Titanium adherends did not perform as well in the -67°F nor the 75°F lap shear tests compared to primed phosphoric acid anodized 2024-T81 or 7075-T6 aluminum. At 350°F, however, bond strength to titanium was adequate; test values for both adhesives readily exceeded specification requirements. Wedge crack extension measurements on titanium slightly exceeded specification maximum allowable values for RB-398 adhesive bonds. AF-131 bonds varied from complete failure upon wedge insertion to complete failure shortly after test exposure. Failures were at the adhesive/primer interface for both AF-131 and RB-398.

4.2.4   FAILURE ANALYSIS -- An instrumental failure analysis was not performed on the water-base primer specimen(s) bondline(s) since this material was neither the primer system of primary interest nor a likely candidate for Phase II scale-up/qualification testing.

A visual observation was made of each bondline with the aid of optical microscopy, and the visually apparent mode of failure was noted. This information is recorded in Tables 4-3 through 4-12. Failure modes ranged from primer failure, to primer/adhesive failure, adhesive/cohesive failure, cohesive failure, and in some cases, to combined primer/adhesive/cohesive failure. The most critical modes of failure with regard to the performance of the primer were primer failure and adhesion failure to the primer.

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Table 4-15 lists the specimens which failed to meet specification requirements. The specimens which performed poorly in an otherwise normal test configuration (lap shear) failed in the primer or at the primer-to-substrate/adhesive interfaces. We could not tell for certain by visual observation the exact nature of the failures. The lower strength adhesive bonds, which resulted in predominantly primer failure, were most often made with AF-131. The adherend type did not appear to be a factor; phosphoric acid anodized 2024-T81, 7075-T6 aluminum, and chromic acid anodized 6A1-4V titanium substrates all had bonds which failed in the primer or at the primer interfaces. When the relatively brittle AF-131 was "softened" at elevated temperatures (350°F), or was "plasticized" by water from 30 days of exposure to salt spray, bond strengths improved significantly and failure modes changed to predominantly adhesive/cohesive. Conversely, RB-398 bonds failed in the primer or at the primer interfaces in the same manner as AF-131 but at substantially higher strength values, which exceeded specification requirements by a good margin (AF-143 performed identically in Task II). Approximately the same high level of strength was maintained with RB-398 bonds at elevated temperature (350°F) and after moisture (30-day salt spray) exposure. The failure mode also changed, to adhesive/cohesive, which also occurred with AF-131 bonds under elevated temperature and moisture exposure environments.

4.2.5   CONCLUSIONS -- The water-base primer selected for Phase I, Task III screening, XEA-9289, performed almost as well in Task III lap shear bonds as it had previously in Task II, but only when bonded with RB-398 adhesive. In contrast, the bonds made with AF-131 in Task III were lower and did not meet specification requirements compared to the higher bond strengths previously developed with AF-143 in Task II tests. Although different lots of primer were used for Task II and Task III tests, the most likely reason for the lower test values obtained with AF-131 in Task III was the lower lap shear strengths developed by current stocks of AF-131. We noted that 3M was unable to develop as high a test value with AF-131 on electrodeposited primed substrates as they could using AF-143, but the AF-131 adhesive met 3M qualification requirements. AF-131 was a discontinued material because of its asbestos content and it

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could not be replaced with fresh material. RB-398 adhesive, on the other hand, was in production use at Rohr. Fresh qualified material was always available during the program.

4.3 ELECTRODEPOSITED PRIMER

Phase I, Task III application and screening of the XA-3995 primer material was initially projected as a relatively simple task. The Task I primer application operation, which was accomplished from a 4-liter beaker (1-gallon) size laboratory apparatus by 3M, was to be scaled up to a 6-gallon tank typical in principle to the 5,000 gallon Lockheed facility shown in Volume III of AFWAL-TR-87-4085 (Figure 4-1).

We anticipated that the major facilities engineering task would begin at the next level of scale-up in Phase II with the 20-gallon tank facility. Both 3M in primer material manufacture scale-up, and Rohr in facilities planning and projected process screening effort, envisioned the 20-gallon facility as the next major hurdle of the program after the successful completion of Task I. In reality, we found it necessary to fully develop the diminutive 6-gallon facility first. As a result, only two controlled electrodeposition priming experiments were conducted during the course of the program. The intervening time was spent improving the 6-gallon facility and performing the required adjustments to the primer bath(s) as they arose from agitation requirements, temperature control, thickness control, shelf life, and solvent loss control. These topics are addressed chronologically as they affected the course of Task III screening.

4.3.1 TANK DESIGN -- The basic concept for the 6-gallon electrodeposition tank was taken from Lockheed's design found in Volume III of AFWAL-TR-87-4085 but was further modified to the configuration shown in Figure 4-2. It was designed and manufactured by Specialty Plastic Company of Los Angeles, California. This tank configuration has been manufactured by Specialty Plastic Company for other companies engaged in electrodeposited primer coatings. The tank was furnished with a small centrifugal pump capable of circulating water at 1 tank volume change per

Figure 4-1. Lockheed Tank Design

Figure 4-2.   Six-Gallon Tank Design

minute. Heat generation was minimal and was controlled by immersing a 4-foot length of return line tubing in a tank of flowing tap water.

The 6-gallon rectangular tank facility differed from the 3M initial 1-gallon cylindrical tank by (1) an increase to 6 gallons versus 1-gallon volume at 3M, and (2) bath circulation created by pumping through a manifold at the bottom of the 6-gallon rectangular tank versus complete agitation/circulation within the 1-gallon cylindrical tank by a motor-driven propeller device. Early in the program, 3M changed to a small centrifugal pump for agitating their 1-gallon tank. Both the Rohr and the 3M tanks were temperature controlled by circulating the contents of the tank by centrifugal pump through an external heat exchanger cooled by tap water, 3M using a standard water-cooled laboratory condenser and Rohr using coiled tubing in a water bath.

4.3.2   FIRST ELECTRODEPOSITED PRIMING EXPERIMENT -- Electrodeposited Primer XA-3995 was shipped to Rohr in 1-gallon containers at 40 percent solids content. The XA-3995 primer concentrate was let down to 10 percent final bath solids by slow addition of deionized (500K ohms) water with a pH of 6.5 while stirring rapidly with a motorized propeller device. The final pH of the let-down primer was 5.1, which remained steady for 15 days. The let-down procedure was supervised by Mr. Tom Wilson of the 3M Company. The diluted primer was maintained under constant agitation until the let-down procedure was finished and the transfer to the 6-gallon tank was completed. After transfer to the 6-gallon tank, it was apparent that the existing centrifugal pump could not pump the primer material because the head pressure was insufficient. Immediate adjustments to the pumping circuit were made by rerouting the pump output from the bottom manifold to a free-flow condition into the top of the tank. The pump circuit flow through the coiled heat exchanger tubing was retained. This arrangement did not create adequate agitation in the tank, so a motorized propeller was placed into the tank as the main source of agitation. The 6-gallon tank, at this point, was essentially in the same operating configuration as the initial 1-gallon 3M tank.

Upon completing the temporary modifications to the circulating/agitation system, the tank was fitted with two 16-inch by 18-inch stainless steel (type 304) anodes, one next to each side of the tank. A Hewlet-Packard HP 6267B power supply producing 0-40 volts DC to 10 amps was fitted to the anodes with the test coupons completing the circuit as the cathode. Trial coatings were then made on phosphoric acid anodized 2024-T81, 7075-T6, chromic acid anodized 6Al-4V titanium lap shear coupons, and phosphoric acid anodized 5052 honeycomb core (1/4-inch cell). The first coatings, which were measured with an isoscope, were found to range in thickness from 0.00015-inch through 0.0035-inch film thickness after cure at 350°F for 2 hours. Visually, the panels seemed to be evenly coated with a good appearance. The time and voltage conditions were varied during the initial coating experiments as follows:

ADHEREND	VOLTAGE	TIME (SECONDS)
Aluminum Panels	30	6 - 10
Aluminum Core	40	15 - 20
Titanium Panels	40	20 - 25

We found that a wide range of primer thickness-versus-time, voltage, and substrate variations was possible and that efforts to define all of these variations would entail a large test matrix at considerable time and expense. We decided, therefore, to select a single voltage (40 volts) and to determine by trial the time interval required to produce a primer thickness of nominally 0.0001-inch cured film thickness. When the required primer film thickness was achieved, the entire complement of test specimens was coated in a continuous sequential manner, in order to simulate the mechanics and processing requirements of a production environment.

4.3.2.1   Bath Stability -- When freshly prepared, the primer bath produced an electrocoat with an excellent quality appearance; however, after 4 days of aging, it was not possible to prime either aluminum or titanium adherends. We made some preliminary determinations to correct the problem with the primer. We found that the conductivity of the primer had changed markedly and that the primer solvents had decreased to

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zero level. The primer bath was replenished with solvent and its conductivity was brought back to the required level. When the proper solvent makeup was maintained, the aluminum details were easily and completely coated with primer. The visual quality of coated and cured parts appeared to be the same as it was at the start of the priming exercise. Solvent loss was attributed to the seal at the propeller shaft used to provide agitation to the tank. The rate of solvent loss versus time and square feet of metal stock coated is given in Table 4-16.

The coating quality of XA-3995 on titanium was not as good as on aluminum details. This may have been due to a difference in the electric conductivity. We found that electropriming of titanium requires different parameters than those for aluminum.

4.3.2.2   Screening Tests -- Concurrent with the priming trials, test specimen configurations per Table 4-2 were laid up and bonded with AF-131 and RB-398 adhesive materials. Both adhesive materials were cured in the laboratory autoclave at 350°F for 1 hour under 35 psi maintained throughout the cure cycle and during cool-down to 180°F. Bonded specimens were tested as soon as possible to assess the primer's effect on as many adhesive bondline parameters as possible within the shortest time span. The results of these tests are noted in Tables 4-17 through 4-24.

4.3.2.3   Test Results -- Table 4-25 is a tabulation of the averaged lap shear data from Tables 4-17 through 4-20 which are below MMM-A-132 or FMS-1013 requirements. A significant number of tests were failing minimum strength criteria, and all work remaining on Task III of the program such as bonding of primed specimens and testing of bonded specimens was terminated pending a resolution of the problem. The first action taken was to measure the primer thickness on as many of the primed specimens as practicable. We found that primer thickness was highly inconsistent across the face of the panel as well as between panels, particularly with regard to the specified nominal thickness of 0.0001-inch to 0.00015-inch maximum. Although the priming trials were begun within the thickness tolerance range, the considerable degree of

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Table 4-16. Solvent Retention as a Function of Bath Usage

DATE	SQ. FT. COATED	SOLVENT-RETENTION IN PRIMER (PERCENT)		
		MIBK	XYLENE	2-BUTOXYETHANOL
6-26-87				
- Fresh	0	100	100	100
- After 8 hours	30	-	-	-
7-1-87	0	0	0	74
7-8-87*	-	100	100	100
7-9-87				
Morning	25	55	76	90
Evening	15	53	74	89

* Replenish the bath

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Table 4-17. Lap Shear Strength Using AF-131 on Phosphoric Acid Anodized/XA-3995 Primed 2024-T81 and 7075-T6 Aluminum

METAL ADHEREND	TEST TEMPERATURE			
	75°F (PSI)		350°F (PSI)	
2024-T81 ALUMINUM	2080		2660	
		2240		2570
	2140		2650	
		2170		2610
	2360		2760	
		2270		2730
	$\bar{x}$	2210		2660
	Sx	101		74.1
	%	4.6		2.8
7075-T6 ALUMINUM	2670		2740	
		2510		2120
	2470		2570	
		2520		2230
	2380		2820	
		2580		2310
	$\bar{x}$	2520		2460
	Sx	99		290
	%	3.9		11.8

NOTES: - Data rounded to ±5

- Phosphoric Acid Anodized Aluminum

Table 4-18. Lap Shear Strength Using AF-131 on Chromic Acid Anodized/XA-3995 Primed 6Al-4V Titanium

ADHEREND		TEST TEMPERATURE	
		75°F (PSI)	350°F (PSI)
Ti-6Al-4V PRIMED @ ROHR		1990	1800
		2150	1610
		2230	1810
	$\bar{x}$	2120	1740
	Sx	126	113
	%	5.9	6.5
Ti-6Al-4V PRIMED @ 3M		2360	1700
		2330	1690
		2140	1700
		2250	2010
		2620	1690
	$\bar{x}$	2340	1760
	Sx	179	141
	%	7.6	8.0

NOTES: – Data rounded to ±5
        – 5V Acid Anodized Titanium

Table 4-19. Lap Shear Strength Using RB-398 on Phosphoric Acid Anodized/XA-3995 Primed 2024-T81 and 7075-T6 Aluminum

METAL ADHEREND	TEST TEMPERATURE					
	-67°F (PSI)		75°F (PSI)		350°F (PSI)	
2024-T81 ALUMINUM	3510		3540		1870	
		2900		3640		900
	2780		3220		1410	
		3100		3710		957
	3310		3520		1540	
		3400		3030		1080
	$\bar{x}$	3170	3440		1290	
	Sx	219	261		378	
	%	9.2	7.6		29.2	
7075-T6 ALUMINUM	3590		3300		1890	
		2890		3340		1810
	3050		3440		1800	
		2460		3540		1870
	3500		3370		1820	
		2800		3810		1350
	$\bar{x}$	3050	3460		1760	
	Sx	429	187		201	
	%	14.1	5.4		11.4	

NOTES: - Data rounded to ±5
- Phosphoric Acid Anodized Aluminum

**Table 4-20. Lap Shear Strength Using RB-398 on Chromic Acid
Anodized/XA-3995 Primed 6Al-4V Titanium**

ADHEREND	TEST TEMPERATURE					
	-67°F (PSI)		75°F (PSI)		350°F (PSI)	
Ti-6Al-4V PRIMED @ ROHR	1590		1190		1590	
		1220		1100		1790
	1810		2010		1520	
		1670		1520		1830
	1300		2260		1710	
		1670		1370		1620
	x̄	1550	1580		1680	
	Sx	232	466		119	
	%	15.04	29.6		7	
Ti-6Al-4V PRIMED @ 3M	2730		3530		1510	
		2710		3470		
	2960		3800		1640	
		2540		3410		1580
	2570		3570		1640	
						1500
	x̄	2700	3560		1570	
	Sx	164	151		65	
	%	6.1	4.2		4.2	

NOTES: - Data rounded to ±5
- 5V Chromic Acid Anodized Titanium

Table 4-21. Sandwich Flatwise Tensile Strength (1/4-Inch Cell)
Using AF-131, RB-398 on Phosphoric Acid Anodized/
XA-3995 Primed 2024-T81 and 7075-T6 Aluminum

ADHESIVE TEST TEMP.	METAL ADHERENDS			
	2024-T81 (PSI)		7075-T6 (PSI)	
AF-131 325°F	1120		974	
		1040		940
	1010		933	
		1080		1050
	1040		913	
	$\bar{x}$	1060	962	
	Sx	44.2	52.5	
	%	4.2	5.5	
RB-398 75°F	1190		1320	
		1330		1270
	1140		1310	
		1180		1230
	1240		1210	
	$\bar{x}$	1220	1270	
	Sx	75.4	46.2	
	%	6.2	3.6	
325°F	---	---	672	
				657
			657	
				662
			629	
			$\bar{x}$	655
			Sx	16.1
			%	2.45
-67°F	---	---	1240	
				1420
			1450	
				1360
			1390	
			$\bar{x}$	1370
			Sx	81.3
			%	5.9

Table 4-22. Sandwich Climbing Drum Peel Strength (1/4-Inch Cell) Using AF-131, RB-398 on Phosphoric Acid Anodized/ XA-3995 Primed 2024-T81 and 7075-T6 Aluminum

ADHESIVE TEST TEMP.	METAL ADHERENDS			
	2024-T81 LB/3 INCH		7075-T6 LB/3 INCH	
AF-131 75°F	18.1		9.2	
		11.8		13.2
	13.7		9.5	
		11.4		13.6
	12.9		9.5	
		11.1		12.8
	x̄	13.2	11.3	
	Sx	2.6	2.1	
	%	19.9	18.7	
RB-398 75°F	24.9	x̄ 25.9	31.4	x̄ 30.7
	24.5	Sx 2.1	30.3	Sx 0.6
	28.4	% 8.2	30.3	% 1.9
180°F	23.7	x̄ 24.0	20.0	x̄ 19.5
	24.3	Sx 0.3	18.8	Sx 0.61
	24.1	% 1.2	19.7	% 3.1
-67°F	31.7	x̄ 30.3	32.2	x̄ 30
	28.1	Sx 1.9	30.2	Sx 2.3
	31.1	% 6.4	27.7	% 7.6

Table 4-23. Wedge Crack Propagation Test Results Using AF-131, RB-398 on Anodized/XA-3995 Primed Metal

ADHEREND TYPE	WEDGE CRACK PROPAGATION (INCHES) AFTER 2 HOURS AT 140°F/95-100%	
	ADHESIVE AF-131	ADHESIVE RB-398

2024-T81 ALUMINUM	0	0.005
		    0.048
		0.015
		    0.065
		0.044
		
		Ave. 0.0344

7075-T6 ALUMINUM	0	0.00
		    0.043
		0.035
		    0.028
		0.090
		
		Ave. 0.0392

6A1-4V TITANIUM	0	0

Table 4-24. Room Temperature T-Peel Strength Using RB-398 on Phosphoric Acid Anodized/XA-3995 Primed Metal

METAL ADHEREND	T-PEEL (LB/IN)			
2024-T81 ALUMINUM	34.6			
		24.9		
	74.7			
		79.7	$\bar{x}$	63.7
	72.3		Sx	34.1
		123.0	%	53.5
7075-T6 ALUMINUM	6.4			
		7.0		
	8.8		$\bar{x}$	7.7
		7.2	Sx	1.15
	9.0		%	14.9
6A1-4V TITANIUM	FAILED PRIOR TO TESTING			

Table 4-25. Reconcilation of Tables 4-17 through 4-20
Averaged Lap Shear Strength with
MMM-A-132 and FMS-1013 Requirements

ADHEREND	ADHESIVE	TEST TEMP	LAP SHEAR, PSI	REQUIREMENT	
2024-T81	AF-131	75°F	2210	2750	(1)
	RB-398	350°F	1290	1800	(2)
7075-T6	AF-131	75°F	2520	2750	(1)
	RB-398	350°F	1760	1800	(2)
Ti-6A1-4V	AF-131	-75°F	2120	2750	(1)
		350°F	1740	1800	(2)
Ti-6A1-4V	RB-398	-67°F	1550	2750	(1)
		75°F	1580	2750	(1)
		350°F	1680	1800	(2)

(1) MMM-A-132 Requirement

(2) FMS-1013 Requirement

variation which occurred throughout the Task III priming experiment suggests that the experiment was started by initially achieving a coating thickness value within tolerance apparently by coincidence. The primer thickness range measured for the various substrates coated is given in Table 4-26.

At the onset, titanium was a difficult material to prime to the required 0.0001-inch to 0.00015-inch thickness range. We decided to proceed with bonding and testing of the titanium specimens which had been primed on a best effort basis. In this exercise, 3M contributed titanium specimens which they had primed according to their own criteria. Both Rohr- and 3M-primed titanium coupons exceeded the required 0.0001-inch to 0.00015-inch thickness range by Rohr measurement. To verify these measurements, Rohr measured test specimens supplied by 3M and verified 3M's previous measurements.

In general, 3M-primed titanium panels varied in thickness from slightly out of tolerance to about 55 percent beyond maximum tolerance; whereas none of the Rohr-primed panels were within 43 percent of maximum tolerance, some as great as 117 percent out of maximum tolerance. This thickness variability appears to be reflected in the lap shear strength values given in Tables 4-18 and 4-20. The 3M panels did very well on the 75°F lap shear test and came very close to passing the -67°F test requirement (Table 4-20); whereas the Rohr-primed panels failed to meet MMM-A-132 lap shear strength requirements in all test configurations. The higher lap shear strength values reached by some of the 3M specimens is probably due to the thinner primer thickness on this series of specimens; however, we were unable to verify this assumption.

4.3.2.3.1 Failure Analysis -- As previously noted, several of the test configurations bonded with AF-131 and RB-398 on XA-3995 primed 2024-T81, 7075-T6 aluminum, and 6V-4Al titanium failed to develop strength values which met MMM-A-132 requirements. Also, the strengths of Rohr test data were not comparable to 3M data generated on the program. From visual microscopy, it was apparent that some type of interfacial condition existed and that adhesive strength (cohesive rupture) generally was not a

Table 4-26. Primer Thickness (Mils) of Lap Shear Specimens Anodized and Primed with XA-3995

METAL ADHERENDS	PRIMER THICKNESS (MILS)	
	AVE. OF 12 SPECIMENS	RANGE MIN. - MAX.
1. 2024-T81 Al	0.168	0.106 - 0.254
2. 7075-T6 Al	0.177	0.112 - 0.258
	AVE. OF 5/6 SPECIMENS	RANGE MIN. - MAX.
3. 6Al-4V Titanium		
- Rohr Primed	0.260	0.214 - 0.325
- 3M Primed	0.204	0.166 - 0.233
4. 6Al-4V Titanium Wedge Crack Specimens	0.177	0.164 - 0.195

factor. In an attempt to determine whether or not the primer or anodize surface treatments were faulty, several specimens, some exhibiting nominal and others very low bond strengths, were examined at Rohr using scanning electron microscopy complemented with energy dispersive spectrometry. A model DS-130 ISI SEM instrument outfitted with a Model 9900 windowless EDAX attachment was used. In general, the procedures outlined by G.T. Beckwith in AFWAL-TR-82-4171 were used except that total magnification was limited on the Rohr equipment because of local magnetic disturbances. Cryocracking/high magnification examination of the oxide layer was not practical.

The specimens examined were as follows:

Specimen #1, 2024-T81 aluminum adherend bonded with RB-398 adhesive, was from a group which had an average failing stress of 1290 psi at 350°F (Table 4-19). The failure mode f this specimen was principally through the primer layer.

Specimen #2, 2024-T81 aluminum adherend bonded with AF-131 adhesive, was from a group which had an average failing stress of 2660 psi at 350°F (Table 4-17). The failure mode of this specimen was combined cohesive and interfacial through the thin primer, oxide, and to the substrate interface.

Specimen #3, 7075-T6 aluminum adherend bonded with AF-131 adhesive, was from a group which had an average failing stress of 3050 at -67°F (Table 4-19). The failure mode of this specimen was combined cohesive and interfacial at/through the aluminum oxide/primer interface.

Specimen #4, 6Al-4V titanium adherend bonded with RB-398 adhesive, was from a group which had failed during cutting. The failure mode of this specimen was predominantly in the oxide layer.

Specimen #5, 2024-T81 aluminum adherend bonded with AF-131 adhesive by 3M, failed at 2866 psi. The failure mode of this specimen was

predominantly cohesive with some interfacial failure at/in the oxide/adherend interface.

A more detailed description of the above failure analysis is given in Appendix D.

4.3.2.3.2 Failure Assessment

1) Specimen #5, fabricated by 3M under controlled laboratory conditions, was a visually normal lap shear specimen because the predominant failure mode was cohesive. Where interfacial failures were seen, as in the oxide layer within itself or to the adherend, they were readily apparent. The failure of the primer layer could be its lack of adhesion to the anodize layer, but our instrumentation or technique is not sufficiently sensitive to verify this.

2) The failure of the titanium specimen bonded by Rohr appeared to fail principally in the oxide layer.

3) The remaining specimens, bonded under simulated production conditions, revealed a variety of bondline inconsistencies such as primer thickness, texture, and interfacial failure mode. None of these conditions appear to consistently cause reduced bond strength performance. The sampling base, however, was very limited, and a much larger sampling would have revealed more definitive relationships for the anomalies seen.

4.3.2.4 Six-Gallon Tank Modification -- The electrodeposition equipment was suspect as a contributor to the variations in primer film thickness and subsequent effect on bond strength. The following

equipment deficiencies seemed to contribute to the problem and were corrected accordingly.

1) **Primer Agitation** -- 3M cautioned that the primer must be kept in constant agitation to prevent corrosion resistant pigment dropout. We decided to abandon the makeshift propeller agitator and return to the Lockheed design entirely by installing a centrifugal pump which developed sufficient head pressure and capacity to allow up to three volume changes per minute. The pump output was controllable from zero to three changes per minute.

2) **Temperature Control** -- 3M recommended tighter limits on temperature fluctuations which may have occurred in the initial priming trials. Unfortunately, autographic temperature monitoring was not in place at that time. It appears that the primer thickness variations may have been due to a gradual increase in temperature as the priming operation continued, causing a higher primer deposition rate to occur. With the reoutfitting of the 6-gallon tank with a 1/2-hp centrifugal pump, very significant temperature increases occurred which could not be tolerated (75°F in 3 hours). This condition was remedied by replacing the existing coiled plastic tube heat exchanger with a much larger stainless steel unit cooled by a constant temperature refrigeration unit. With this modification, the primer bath was maintained at 70 ±1°F under constant circulation of three volume changes (adjustable to five) per minute.

3) **Solvent Loss** -- This situation was improved significantly by replacing the cover which accommodated the agitator propeller shaft with a solid acrylic plate and securing the plate to the tank lip with sealant while the tank was not in use.

4) **Control of Priming Time** -- At 3M's recommendation, the practice of manually timing the primer application was replaced with an automated synchronous motor electric timer device. To effect the primer tank modifications, it was necessary to remove the primer bath. It was impractical to keep the primer in motion and thus prevent settling or control temperature or solvent loss. The bath was abandoned, since it was currently suspect and would continue to be suspect for any future reuse. A new batch of fresh primer concentrate was obtained and placed into 40-degree cold storage. The old batch was used for proving the tank modifications.

4.3.2.5   Six-Gallon Tank Design Verification -- After the 6-gallon tank modifications were completed as described in 4.3.2.4, the tank was fully functional. The old primer bath was circulated for approximately two weeks to ensure that there were no volume/solvent losses, solids dropout, solution separation nor temperature fluctuations. No adverse conditions were found during the trial period. When the 6-gallon tank was ready for use, the old primer bath was removed and the tank prepared to accept the new primer bath. The configuration of the 6-gallon tank at this time was shown in Figure 4-3.

4.3.2.6   Twenty-Gallon and 200-Gallon Tank Design and Fabrication -- Also during this time, considerable work was accomplished in the design and fabrication of the 20-gallon and the 200-gallon tanks for the program. The design of these tanks again closely followed the Lockheed design philosophy featuring a vee bottom with input manifold, end location for the overflow weir, centrifugal pump circulation/agitation (up to one volume change/minute), and heat exchanger. The actual tank dimensions were governed more by the intended use than by any effort to produce a scale equivalent of the Lockheed design. The 20-gallon tank had sufficient depth to accommodate holding fixtures for multiple-specimen priming. The 20-gallon tank was scheduled to be used during Phase II where approximately 1000 specimens were scheduled to be primed.

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6-Gallon Cell

Schematic

E.D. Tank (1)

(5)
Valve

Pump (2)

Chiller (4)

(3) Heat Exchanger
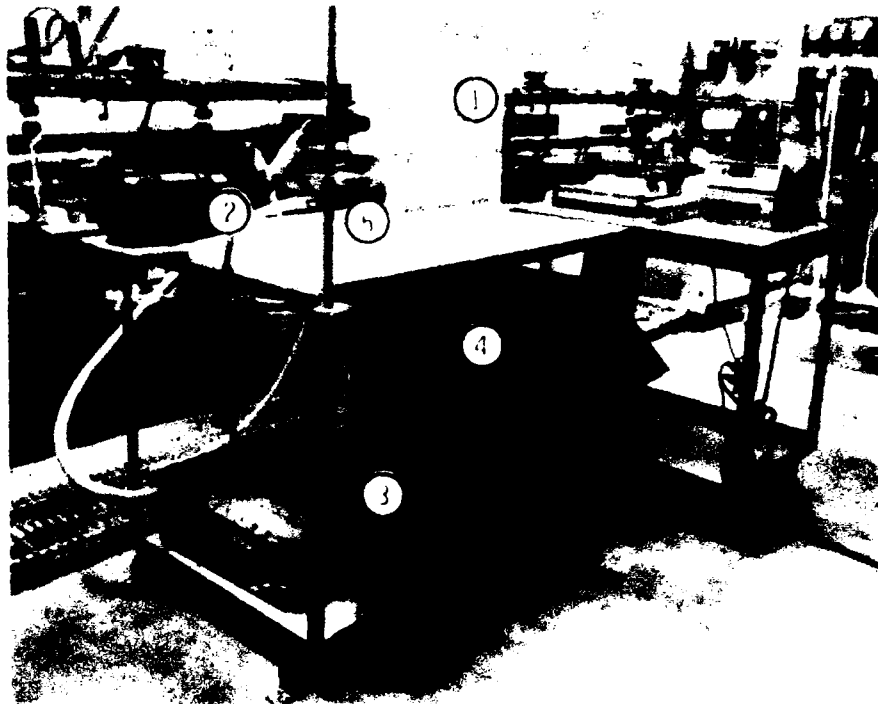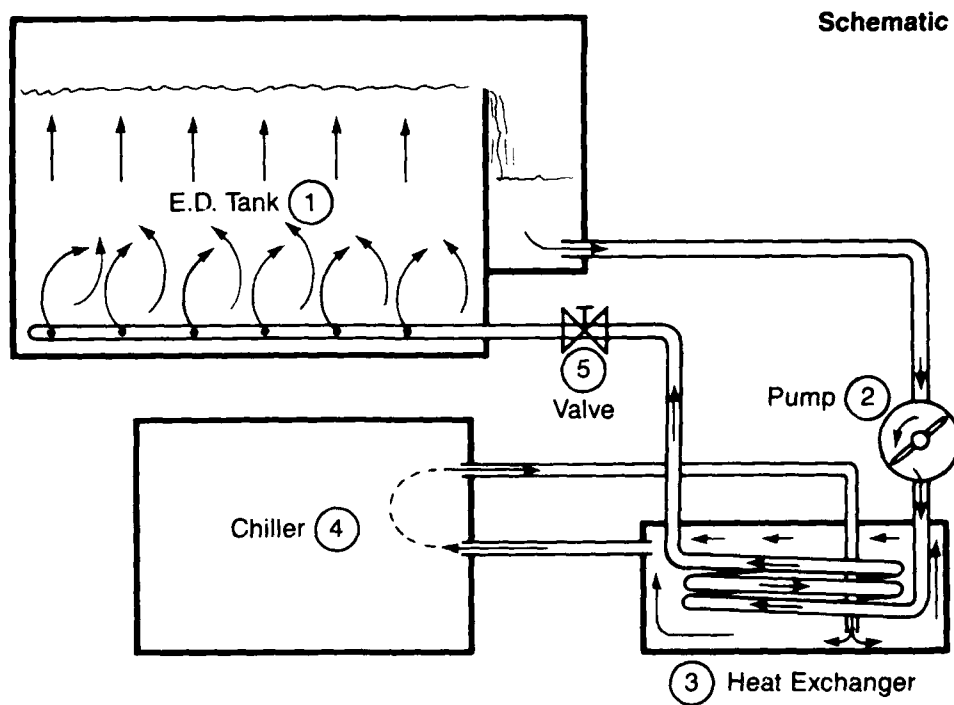
Figure 4-3. Electrodeposition Cell Facility

The design of the 200-gallon tank had sufficient width to handle small production-size details. Although Task III of Phase II of the contract did not require the priming of any details approaching the size capability of the tank, a substantial investment would have been made upon completing the 200-gallon priming facility. Follow-on priming studies were anticipated for this Rohr-funded facility. Photographs 4-1 and 4-2 show the 20-gallon and the 200-gallon tanks in their as-fabricated state.

4.3.3   SECOND BATCH TRIAL -- The second batch of primer concentrate had been stored for several months while modifications to the 6-gallon tank were being completed. Although it was originally intended that a fresh batch of primer would be used for the primer verification tests, the availability of aged primer material was an unexpected opportunity to view the effects of extended storage. The let-down of the second batch of primer was performed under the supervision of Dr. Pocius, 3M Program Manager. The primer concentrate looked very good and let-down as expected according to Dr. Pocius. Dr. Pocius was satisfied by the agitation/circulation rate established (approximately two volume changes per minute). During Dr. Pocius' visit, several lap shear panels were coated with the freshly prepared primer. Although excellent coatings were obtained, we noted that some of the panels were variegated in appearance when primed at the lower coating voltages.

4.3.3.1   Primer Bath Analysis -- The analysis of the second primer batch the day after let-down was as follows:

Solids Content	9.3 %
pH	5.5
Solvent Content (wt. %)	
Mibk	1.46
Xylene	0.98
Butoxy Ethanol	2.60

4.3.3.2   Trial Coating, Second Batch of Primer -- Trial coatings were made on phosphoric acid anodized 2024-T81 and 7075-T6 aluminum lap shear panels (4-inch x 6-inch) in order to establish the voltage and time
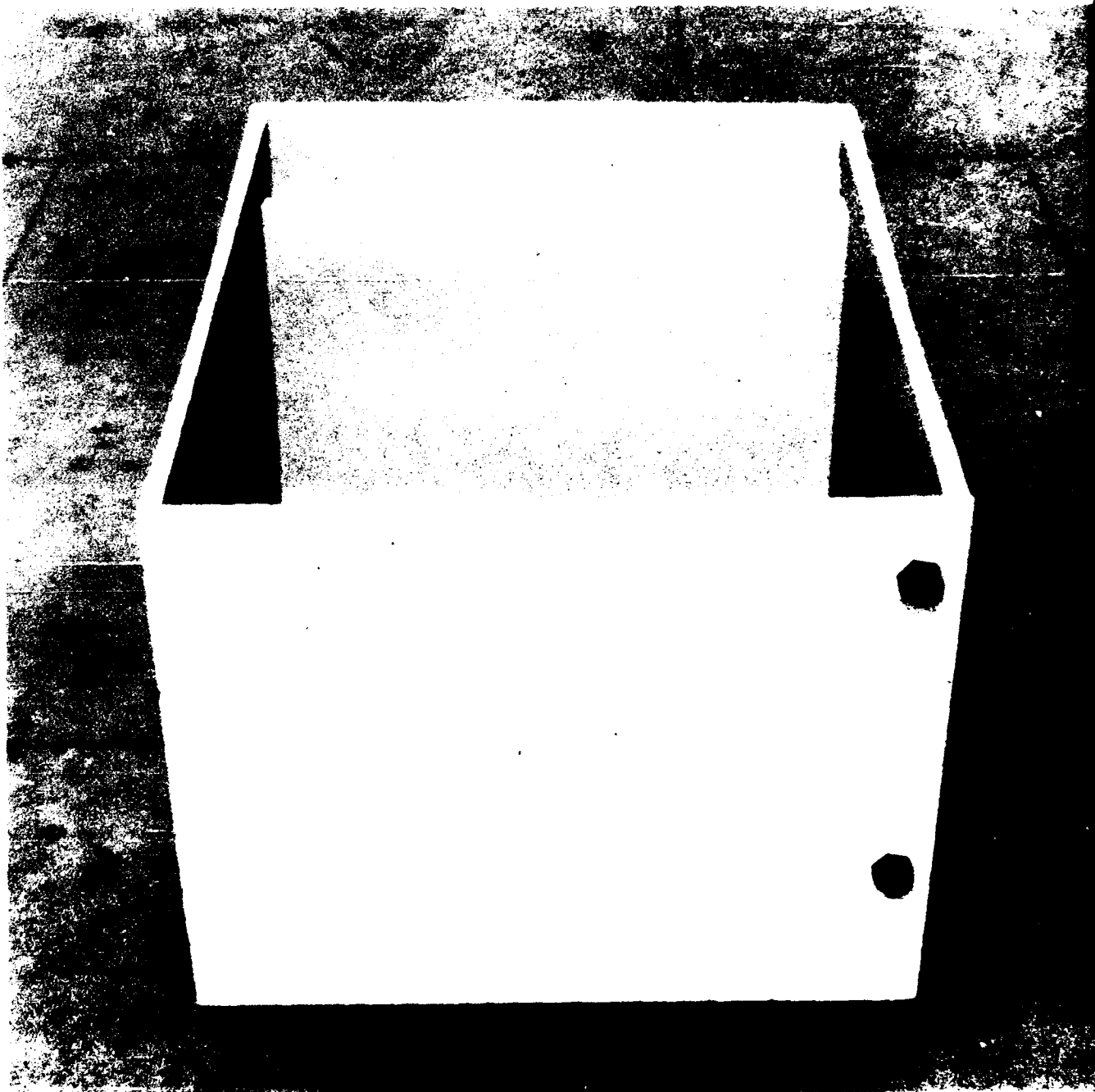
Photograph 4-1. 20-Gallon Tank - End View
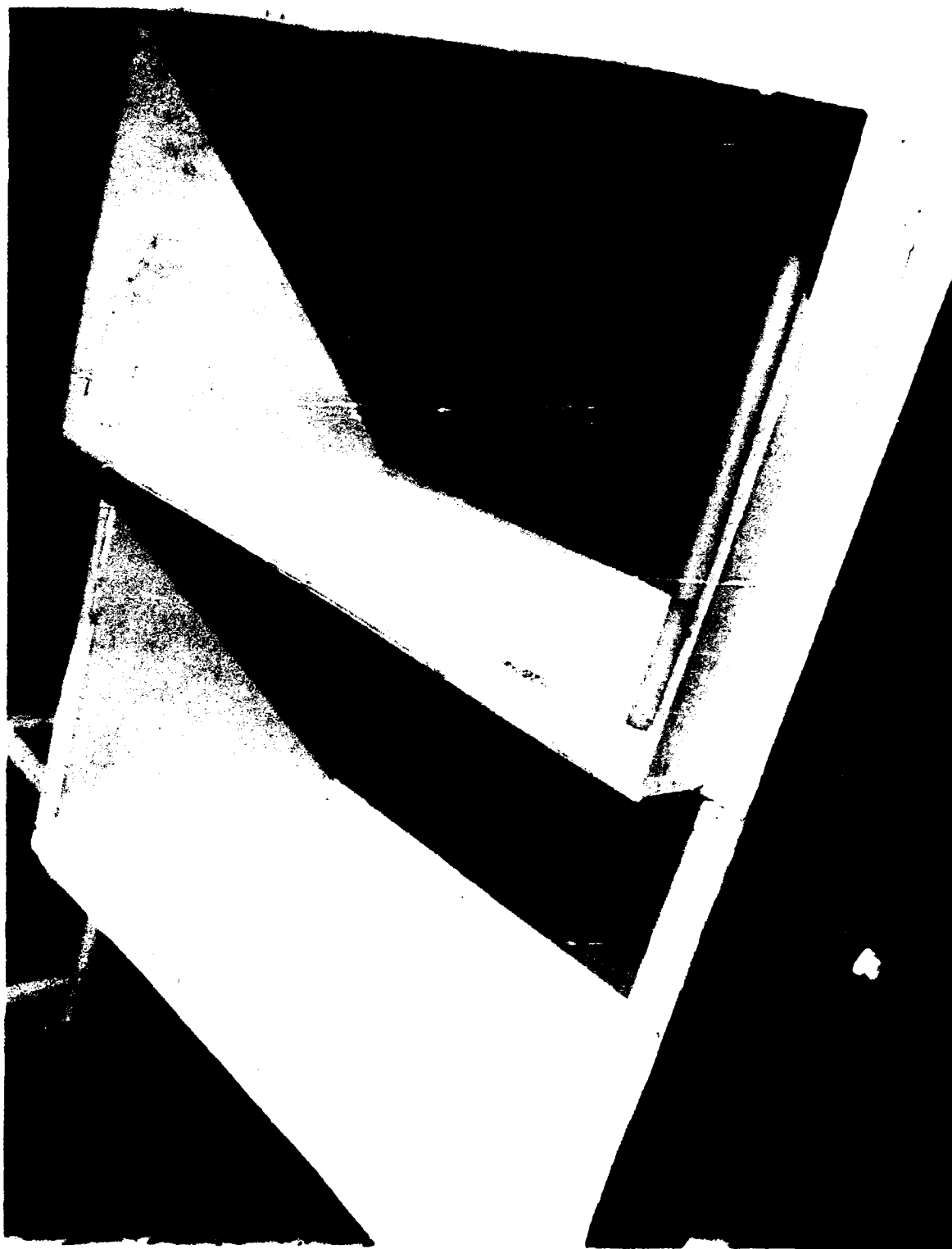
Photograph 4-2.   200-Gallon Tank - Top View

parameters for priming the verification test panels. The coating thickness trial panels were primed at 10-volt intervals from 20 to 40 volts for 5- and 10-second periods. After priming, the panels were air-dried at ambient for 20 minutes followed by an elevated temperature cure for 60-70 minutes at 350°F-355°F in a circulating air oven. After cool-down, 12 readings were taken in grid pattern across the surface of each panel with an "isoscope" thickness-measuring instrument. The averaged results of these time/voltage thickness measurements are shown in Figure 4-4. The priming parameters developed from Table 4-27 data are:

ALLOY	VOLTAGE	TIME (SECONDS)
2024-T81	30	5-10
7075-T6	30	10

A second set of specimens from the primer thickness versus time and voltage determination were sent to 3M for observation and comment. The primed 2024-T81 panels were reported by 3M to be of proper quality. The primed 7075-T6 panels, however, were reported to be somewhat irregular in thickness. 3M also stated that because all of their prior electrodeposition priming experience was with the 2024 alloy, they could not comment on the primer condition seen on the 7075 alloy nor on how this condition might affect bond strength.

Approximately 1 week after the completion of the determination of priming parameters, a number of phosphoric acid anodized 2024-T81 lap shear panels were primed for preparing verification test panels. During the priming of these specimens, we noted that excess primer build-up was occurring at the edges of the panels. Consulting with 3M, we learned that this condition could be due to excessive ion build-up (corrosion resistant pigment dissolution) or pH change. A similar experience was reported by 3M during Phase I, Task I primer optimization work. The net effect of this situation was that the panels could not be coated uniformly within the required primer thickness tolerance of 0.0001-inch nominal, 0.00015-inch maximum. Although the primer bath was fresh regarding let-down from the concentrate within the past two weeks, the

4-51
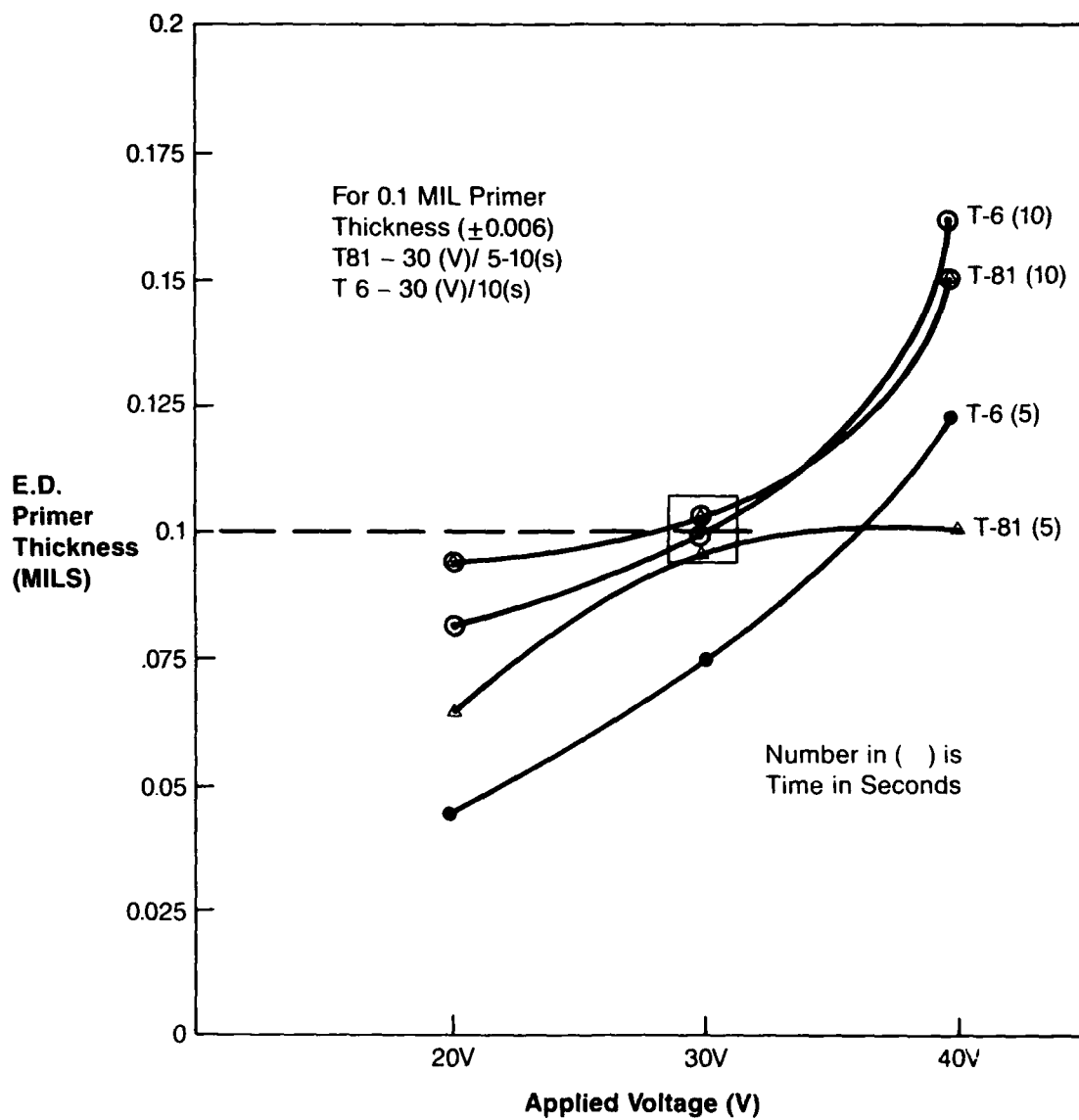
Figure 4-4. Voltage Time vs. Primer Thickness Measurements of E.D. Primer XA-3995 Primed on 2024-T81 and 7057-T6 Aluminum

Table 4-27. Voltage Time Versus Primer Thickness Measurements of XA-3995 Primed 2024-T81 and 7075-T6 Aluminum

VOLTAGE - TIME (V) (SECONDS)	PRIMER THICKNESS (MILS)*	
	2024-T81	7075- T6
20V - 5(s)	0.060 0.063 0.060 0.064 $\bar{X}$ 0.62 S_x 0.0021 $\%^X$ 3.3	0.045 0.047 0.036 0.041 $\bar{X}$ 0.042 S_x 0.0048 $\%^X$ 11.5
20V -10(s)	0.094 0.093 0.099 0.086 $\bar{X}$ 0.090 S_x 0.0053 $\%^X$ 5.8	0.092 0.082 0.072 0.086 $\bar{X}$ 0.083 S_x 0.0084 $\%^X$ 10.1
30V - 5(s)	0.095 0.093 0.090 0.083 $\bar{X}$ 0.091 S_x 0.054 $\%^X$ 6.0	0.072 0.074 0.071 0.082 $\bar{X}$ 0.075 S_x 0.005 $\%^X$ 6.7
30V -10(s)	0.123 0.107 0.101 0.089 $\bar{X}$ 0.105 S_x 0.014 $\%^X$ 13.5	0.092 0.103 0.110 0.099 $\bar{X}$ 0.101 S_x 0.075 $\%^X$ 7.4
40V - 5(s)	0.102 0.094 0.102 0.099 $\bar{X}$ 0.099 S_x 0.014 $\%^X$ 6.0	0.110 0.103 0.138 0.136 $\bar{X}$ 0.122 S_x 0.0075 $\%^X$ 6.7
40V -10(s)	0.131 0.130 0.144 0.149 $\bar{X}$ 0.138 S_x 0.0095 $\%^X$ 6.8	0.137 0.144 0.174 0.192 $\bar{X}$ 0.162 S_x 0.258 $\%^X$ 15.9

* Each reading is an average of six for both sides of two 4" x 6" panels.

primer concentrate was approximately 6 months old. It is possible that some change had occurred in the aqueous-based concentrate stored at 40°F during the 6-month storage period.

4.3.3.3   Solvent Loss -- During the time that the excessive/irregular thickness problem was being investigated, the problem of solvent loss again became a major factor. At first, we thought that the frequent opening and closing of the tank lid was the principal contributor to this condition. A new lid with a mechanical seal and hold-down clamps was fitted to the tank. This addition made it practical to remove and replace the lid rapidly.

Although the redesigned tank lid helped reduce the solvent loss, only a minor improvement resulted. The major cause of solvent loss was soon discovered by the strong odor emanating from the heavy wall vinyl tubing used to plumb the 6-gallon tank to the pump and heat exchanger units. The vinyl tubing had been in service for several months during the outfitting of the pump units and had not shown any indication of solvent leakage. This was apparently due to the low solvent content remaining in the old batch of primer used for the equipment checkout, and later to the length of time required for the solvents to diffuse through the thick vinyl tubing wall after the primer had been placed in the tank. All of the vinyl tubing plumbing was then removed and replaced with standard polypropylene pipe and fittings, which immediately stopped the leakage.

The pump was adjusted to achieve adequate circulation (approximately two volume changes/minute). The proper solvent content was reestablished and the tank sampled over a 12-day interval. The results of sampling tests are shown in Table 4-28. The sampling period indicated that the major solvent loss problem had been corrected and that a periodic solvent replenishment schedule could be established. A Hewlett-Packard gas chromatograph was used for the solvent analysis.

4.3.3.4   Dialysis -- The recommended solution to the thickness control problem was to dialyze the primer bath as 3M had successfully done in

Table 4-28. Solvent Content versus Time for Six-Gallon
Electrodeposition Cell Batch No. 2, XA-3995

SOLVENT	NOMINAL WT % *	SAMPLING DATE			
		4/21/88	4/25/88	4/28/88	5/02/88
MIBK	1.46	0.61	1.47	1.46	1.48
XYLENE	0.91	0.14	0.61	1.81	0.93
BUTYL CELLUSOLVE	2.41	2.52	1.79	2.60	2.99

* Normal tolerances +3.0% to -0.5%

Phase 1, Task 1. Rohr investigated dialysis treatment as a probable requirement for scale-up as a result of 3M's earlier finding of coating irregularities after their primer bath had been in service for 50 days. Also, dialysis was reported to be a normal primer bath maintenance requirement for electrodeposited paints used by the automotive industry. Although Rohr had previously begun inquiries into ultrafiltration/ dialysis procedures and equipment for possible applications on the 200-gallon tank, we did not find in our survey any source of ready-made equipment which could be fitted to our 6-gallon tank. All dialysis capability located required that the equipment be designed for the particular makeup of the primer formulation used. This involved significant cost and lead time and was intended for use on tanks several magnitudes greater in size. We elected, therefore, to attempt to duplicate the same rudimentary dialysis procedure used by 3M on their 1-gallon tank.

The Rohr tank, with associated plumbing for the pumping and cooling circuits, approximated ten times the volume of primer as the 3M tank. In order to achieve the same relative dialysis time, our first dialyzer incorporated a circular chamber into which 20 feet of the same Spectra/Por 6 dialysis membrane tubing used by 3M was coiled in a special double-deck holding fixture. This arrangement gave the same relative dialysis efficiency as 3M achieved by their 2-foot length of tubing for 1 gallon of primer. Unfortunately, the 20-foot length of Spectra/Por 6 tubing contained numerous defects which resulted in rupture and loss of primer.

The circular dialysis tank with its spiral holding fixture for the dialysis tubing was abandoned in favor of three troughs each holding a 3-foot to 4-foot length of dialysis tubing. This arrangement made it easier to hook up the dialysis tubing and made useful shorter lengths of tubing.

After the three-trough dialysis equipment was in place (Figure 4-5) and refitted with the improved-strength Spectra/Por 600 dialysis tubing, the dialysis experiment was restarted and run for 54 hours. During this

4-56

E.D. Primer Tank   **Schematic**

Gravity Feed
Dialysis Tray

Pump

Collector
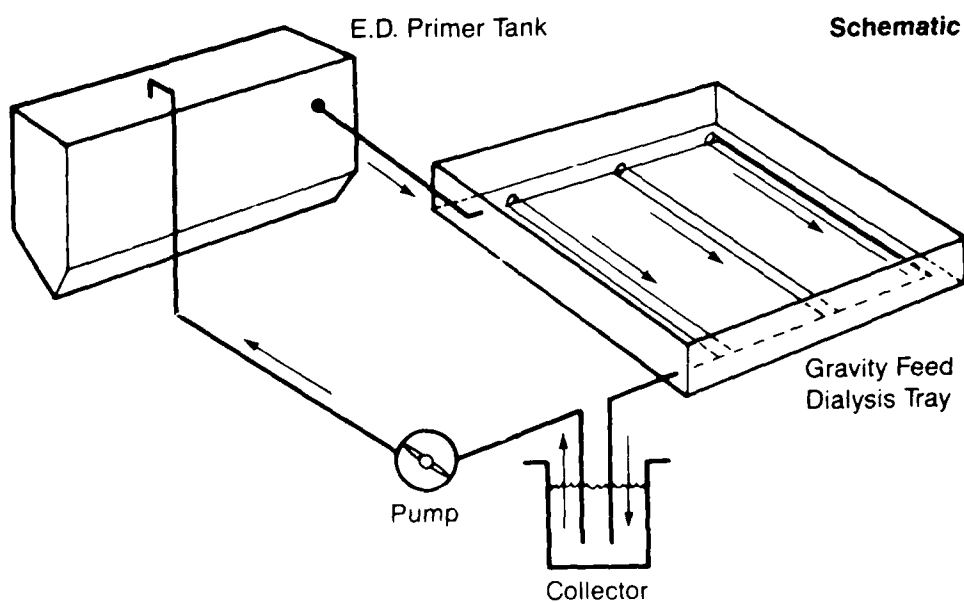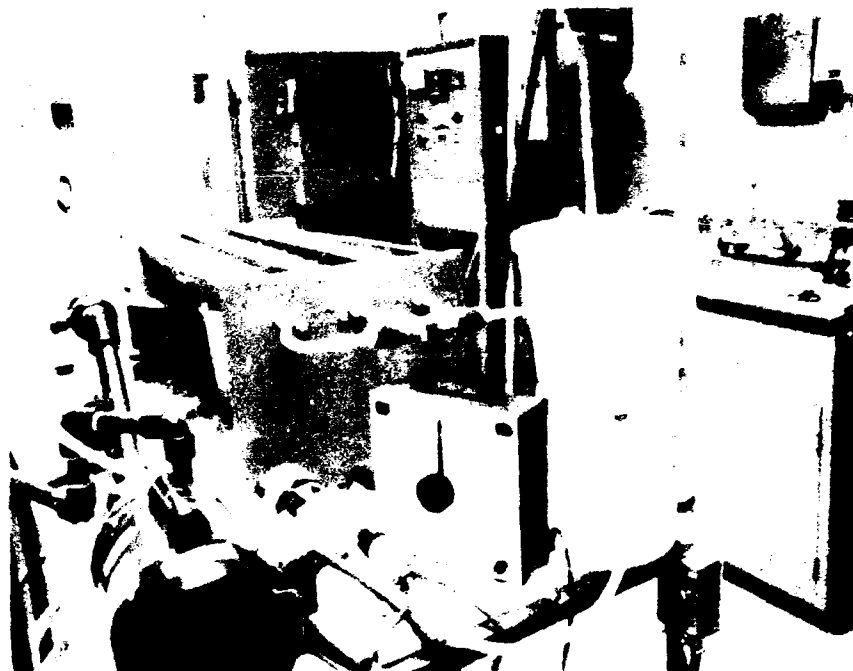
Figure 4-5.   Six-Gallon Electrodeposition Cell Facility
with Dialysis Setup

time, a significant change was noted in the appearance of the primer bath; it also had a tendency to foam on exit from the return line coming from the dialysis fixture. The return line was powered by a small 1/7-hp centrifugal pump which may have been cavitating. The change in appearance of the primer bath, from light straw-yellow/cream color to a dirty yellow/milkish color, was due to excessive solvent loss. During the relatively short dialysis period, the major portion of the primer bath solvent content appeared to have been lost as a result of dialysis. At the end of the dialysis period, the primer bath was analyzed and replenished to proper solvent content.

4.3.3.4.1 Effect of Dialysis on Primer Thickness -- Table 4-29 gives the change in pH and resistance of the primer bath with dialysis time. The data indicate that the resistance and the pH of the primer bath was not changed significantly by dialysis. Following the replenishment of the primer bath with the required solvents, another priming trial was made on phosphoric acid anodized 2024-T81 lap shear panels. These panels were primed at 30 volts for 7-second and 10-second time intervals. The electrodeposited primed panels were given the normal deionized water rinse, 20-minute ambient temperature air-dry followed by a 350°F cure for 60-70 minutes in a circulating air oven. With a 7-second priming time at 30 volts, the center section of the panel was within thickness tolerance whereas the edges were significantly out of thickness tolerance. Thickness variability within the measured areas was also extensive. Upon increasing the priming time from 7-seconds to 10-seconds, a difference of only 3 seconds, primer thickness increased significantly and was out-of-tolerance at both the center and edges of the panel. A visual examination of the panels at 60X magnification revealed an "orange-peel" surface condition composed of "microcraters," many of which appeared to be quite deep toward the surface of the adherend. We concluded that the dialysis treatment did not appear to have corrected the primer thickness problem.

4.3.3.4.2 Effect of Lactic Acid Addition on Primer Thickness -- Another factor affecting coatability was the pH of the primer bath. To assess this possibility, 90 grams of lactic acid, as recommended by 3M, was

Table 4-29. pH and Resistivity Measurements during and after
            Termination of the Dialysis of E.D. Primer
            Batch No. 2, XA-3995

DATE	HOURS DIALYZED	pH	RESISTIVITY ohm/cm
5/13/88	3.5	4.41	1000
5/16/88	6.0	4.44	1450
5/19/88	20.0	4.48	1100
5/20/88	24.0	4.45	1350
5/23/88	---	4.63*	1650*
	Total = 53.5 Time Hours		

* Measured after adding required amount of solvents

added to the 6-gallon tank at the rate of 20 grams per hour. As a result
of this addition, the pH of the primer increased from 4.63 to 5.33. No
change in the electrical resistance of the bath was seen.

A set of phosphoric acid anodized 2024-T81 lap shear panels was primed in
the lactic-acid treated bath at 30 volts for 7-second and 10-second
durations. The panels were rinsed, dried, and cured at 350°F as before
and the thickness of the primer measured at the center and edges of the
panels with an isoscope. The primer thickness data is given in Table
4-30. Some improvement had occurred as shown by the slight reduction in
total thickness developed at the center and edges of the panel and in the
data scatter within the measured areas compared to the "after-dialysis"
data. Nevertheless, the primer thickness measured for the edge condition
continued to be out-of-tolerance, and the 3-second additional priming
time continued to increase the primer thickness build-up at the edges at
the same rate as before. An additional priming exercise was performed
with the same primer bath to verify a report by 3M that the "orange-peel"
surface condition could be caused by placing the primed panels into a hot
curing oven. We could not verify 3M's results by curing the primed
panels starting with a cold oven; primer thickness variations and
"orange-peel" effects remained as before. Further attempts to prime with
the bath were discontinued. A 1-gallon sample of the primer bath was
sent to 3M for study. 3M was able to reconstitute the 1-gallon sample
with lactic acid and solvent adjustment and to prime with it in their
laboratory tank. Rohr reviewed the coated samples and found some of them
to be fairly evenly coated but rather thin (0.00006-inch to 0.00013-inch)
and extremely porous when tested per Paragraph 4.3.5.1.

4.3.3.5   Effect of Primer on Tank Construction Materials -- The
6-gallon tank and associated plumbing and heat exchanger were emptied of
primer material, then disassembled for cleaning and inspection. A
thorough examination was made to determine if there was any evidence of
deterioration which may have contaminated the primer bath and contributed
to the priming problem. Other than a few "pinched" O-ring seals which
had to be replaced, the equipment appeared to be unchanged. The only
abnormal condition noted was an accumulation of resinous precipitate in

Table 4-30. Primer Thickness of E. D. Primer, XA-3995 Primed on Phosphoric Acid Anodized 2024-T81 Aluminum

I. AFTER DIALYSIS

VOLTAGE-TIME (VOLTS) (SECONDS)		PRIMER THICKNESS (MILS)* @ PANEL LOCATION			
		CENTER		EDGE	
1.	30-7	0.068 0.076	0.144	0.219 0.180	0.286
		$\bar{x}$	0.096	$\bar{x}$	0.228
		S_x	0.042	S_x	0.054
		% C.V.	43.50	% C.V.	23.5
2.	30-10	0.174 0.227		0.325 0.338	
		$\bar{x}$	0.200	$\bar{x}$	0.331
		S_x	0.037	S_x	0.009
		% C.V.	18.7	% C.V.	2.7

II. AFTER TITRATION

		CENTER		EDGE	
3.	30-7	0.09 0.08	0.085	0.18 0.20	0.19 0.14
		$\bar{x}$	0.085	$\bar{x}$	0.177
		S_x	0.005	S_x	0.026
		% C.V.	5.9	% C.V.	14.8
4.	30-10	0.16 0.15	0.12 0.17	0.26 0.28	0.21 0.23
		$\bar{x}$	0.150	$\bar{x}$	0.245
		S_x	0.0216	S_x	0.031
		% C.V.	14.4	% C.V.	12.7

* Each reading is an average of six, for 4" X 6" panels

the bottom of the tank. This material was obviously corrosion resistant pigment and resin which had precipitated from solution/suspension when the solvent content and solution pH went out-of-tolerance during earlier priming trials/dialysis. To verify the corrosion resistant pigment assumption, a qualitative analysis by emission spectrographic technique was performed. The analysis revealed the following:

Major Elements in Precipitated Solids
Zinc

Silicon

Phosphorous

Trace Elements in Precipitated Solids
Magnesium

Iron

Aluminum

Calcium

A similar qualitative analysis by atomic absorptions technique was made on the primer solution supernatant (solids removed by centrifuge) and a portion of the polypropylene material used to construct the tank and plumbing. The intent of this experiment was to determine whether there was any evidence that the tank was being attacked by the primer solution. The analysis revealed the following:

Major Elements in Primer Supernatant
Zinc

Minor Elements in Primer Supernatant
Sodium

Calcium

Major Element in Tank Material (0.82 percent by wt.)
Calcium

Barium

Sodium

Trace Element in Tank Material

Titanium

There is some commonality between the primer supernatant and the filler in the polypropylene tank material because calcium and sodium are present in both materials, but they are probably from separate origins. The absence of any trace of barium in the supernatant or solids precipitate, which is fairly abundant in the tank material, supports this assumption. There does not appear to be any mechanical nor chemical evidence that the tank material was attacked by the primer.

4.3.4   THIRD BATCH TRIAL -- The second batch of primer failed to produce acceptable primer coatings. It did not appear to be salvageable by dialysis nor by pH adjustment. A third batch of primer was procured so that fresh material could be charged into the 6-gallon electrodeposition facility. The facility included the following features:

1)   A direct scaled comparison of the 6-gallon tank width and length to the Lockheed design. Approximately 1-1/2 x 2-1/2 scaled comparison with Lockheed tank depth. An overflow weir, a horizontal distribution manifold along the bottom of the tank with 1/8-inch holes drilled 1 inch on-center on opposite sides and angled parallel with the bottom slope ("V"-shaped bottom) of the tank.

2)   A centrifugal pump which circulated the tank contents in excess of one tank volume change per 8 minutes. The actual capacity of our pump was variable from zero to three tank volume changes per minute.

3)   A heat exchanger that maintained the primer bath temperature at 70"F ±1"F.

4)   Tank construction, plumbing and a tank cover which restricted solvent losses to a level which could be maintained at least

10 days before analysis and makeup were required. A much longer time between makeups may have been practical but had not been proven.

5) An automated timing device to ensure reproducible coating times.

Specimen preparation and priming procedures had been developed and matured during the trials to produce a satisfactory primer coating. From this previous work, a "traveler" or working specification was prepared for defining the work plan to be followed for the third batch priming trial. This "traveler" or work plan is given in Appendix E.

The plan for the third primer batch was to prime and test a partial complement of Phase I, Task III test specimens which, if successful, would provide sufficient data to determine if the program should proceed to Phase II. The partial complement of specimens consisted of the 2024-T81 metal-to-metal and sandwich specimen portion of the Task III matrix (Table 4-2). This, in turn, was further divided sequentially, the metal-to-metal specimens to be primed first followed by the sandwich specimens. The titanium and the 7075-T6 specimen complement of Task III was omitted with Air Force concurrence.

The plan further called for a series of parallel cross-referencing experiments to be performed by 3M personnel using 3M equipment and techniques interchangeably with Rohr equipment and procedures. Mr. Tom Wilson, 3M principal investigator, came to Rohr with various pieces of his apparatus which he set up to interface with Rohr equipment. He also supervised the let-down of the third batch of concentrate and the charging of the 6-gallon tank. The schedule of cross-referencing experiments between Rohr and 3M components were as follows:

1) Phosphoric anodized 2024-T81 panels

2) Power supply

3) Timing instrumentation

4) Electrode (anode) material number (1 or 2) and placement

5) Effect of initial oven temperature (75°F versus 350°F) for curing the primer

6) Simulated 3M priming tank versus the 6-gallon Rohr tank.

4.3.4.1   Trial Coating, Third Batch -- The plan was executed sequentially starting with specimen preparation in accordance with the instructions in Appendix E. The let-down and installation of the third batch of primer which had been freshly formulated by 3M during the previous week was accomplished. Duplicate phosphoric acid anodized 2024-T81 lap shear panels were primed under the various conditions listed. One panel was placed into an ambient temperature oven and the other into a 350°F preheated oven. Both panels were cured for 60-70 minutes at 350°F. On cooling, the primer film thickness was measured across the face with an isoscope, then immersed in tap water containing phenolphthalein indicator and tested for uncoated areas as described in Paragraph 4.3.5.

No discernible difference could be found between the primer films deposited using either the Rohr or 3M equipment (power supply, timer, anode material or phosphoric acid anodized aluminum) nor was there any difference because of starting the primer cure in a cold or preheated oven. The primer film thickness was within the same scatter band for all panels, but all the primer coatings displayed a significant degree of porosity, particularly in areas where the primer film was thin, approximately 0.0001-inch (nominal specification requirement).

Approximately 4 hours after the let-down and charging of the 6-gallon tank had been completed, approximately 2 liters of primer were removed from the 6-gallon tank and placed into a simulated 3M priming cell (4-liter breaker) by Mr. Wilson. After allowing the primer to stand for 1 hour, Tom primed both Rohr and 3M phosphoric acid anodized panels using

Table 4-31. Thickness of XA-3995 (Batch No. 3) Primed Phosphoric Acid Anodized 2024-T81 Aluminum

SIX-GALLON ROHR ELECTROLYTIC TANK			
VOLTAGE-TIME		PRIMER THICKNESS (MILS)	
(Volts)	(Seconds)	(Center)	(Edge)
1. 20	5	0.04	0.089
2. 20	7	0.09	0.114
3. 20	10	0.128	0.153
4. 30	10	0.197	0.260
3M TYPE SETUP (2 LITER) VS ROHR SETUP		PRIMER THICKNESS (MILS)	
20 (Volts) - (7 Seconds)		(Center)	(Edge)
3M, One Anode (Beaker)		0.075	0.113
3M, Two Anodes (Beaker)		0.112	0.144
Rohr, One Anode (6-gallon tank)		0.049	0.064
Rohr, Two Anodes (6-gallon tank)		0.069	0.116

*Each reading is an average of six, for 4" x 6" panels

panels were bonded with RB-398. The test results for the lap shear specimens are given in Table 4-32. The room temperature lap shear results are significantly reduced from test values for XA-3995 primed specimens made earlier in the program. The 350°F test values for XA-3995 primed specimens are approximately the same as the test values for XA-3995 primed specimens made earlier in the program.

Visual examination of the failed 75°F lap shear specimens revealed complete detachment of the primer from the substrate surface. The 350°F lap shear specimens revealed a mixed primer failure with approximately half of the primer remaining on the substrate and the remaining half removed with the adhesive. Visually, it appeared that cohesive failure, the desired failure mode, was not attained.

Other examinations of various primed 2024-T81 phosphoric acid anodized lap shear panels were made using optical and SEM microscopy. The specimens selected for examination were taken from the specimens coated during batch 3 priming experiments. In general, we found evidence of surface tension effects developing during primer cure which resulted in voids in the primer film. The observations made are found in Appendix F.

4.3.5.1   Leakage Test -- A very simple leakage test was devised to qualitatively determine porosity in the primer coatings. The test schematic is shown in Figure 4-6. The classic electrolysis of water reaction which liberates hydroxyl ions and hydrogen gas is used. At the cathode, the electrolysis reaction proceeds as follows in the presence of ionic species.

$$4 \ H_2O + 4 \ \bar{e} \ \text{---}> \ 2H_2 + 4 \ OH^- \tag{1}$$
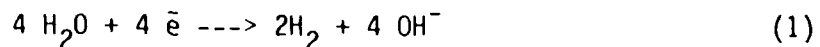
The test makes use of phenolphthalein indicator in the aqueous test cell to detect leakage. As soon as the electrolysis occurs, the OH^- ions generated increase the pH at the leakage site causing the phenolphthalein indicator to turn a very bright red color (pH 9). Leakage sites are readily identified by the red dots occurring over the surface.

Table 4-32. Lap Shear Strength Using RB-398
Adhesive on Phosphoric Acid
Anodized/XA-3995 Primer 2024-T81
Aluminum

75°F		350°F	
2820	3070	1320	1320
3030	2930	1300	1260
2850	-	1310	-
$\bar{X}$	2940 psi	$\bar{X}$	
S_x	110 psi		1300 psi
Var %	3.71%	S_x	25 psi
		Var %	1.9%
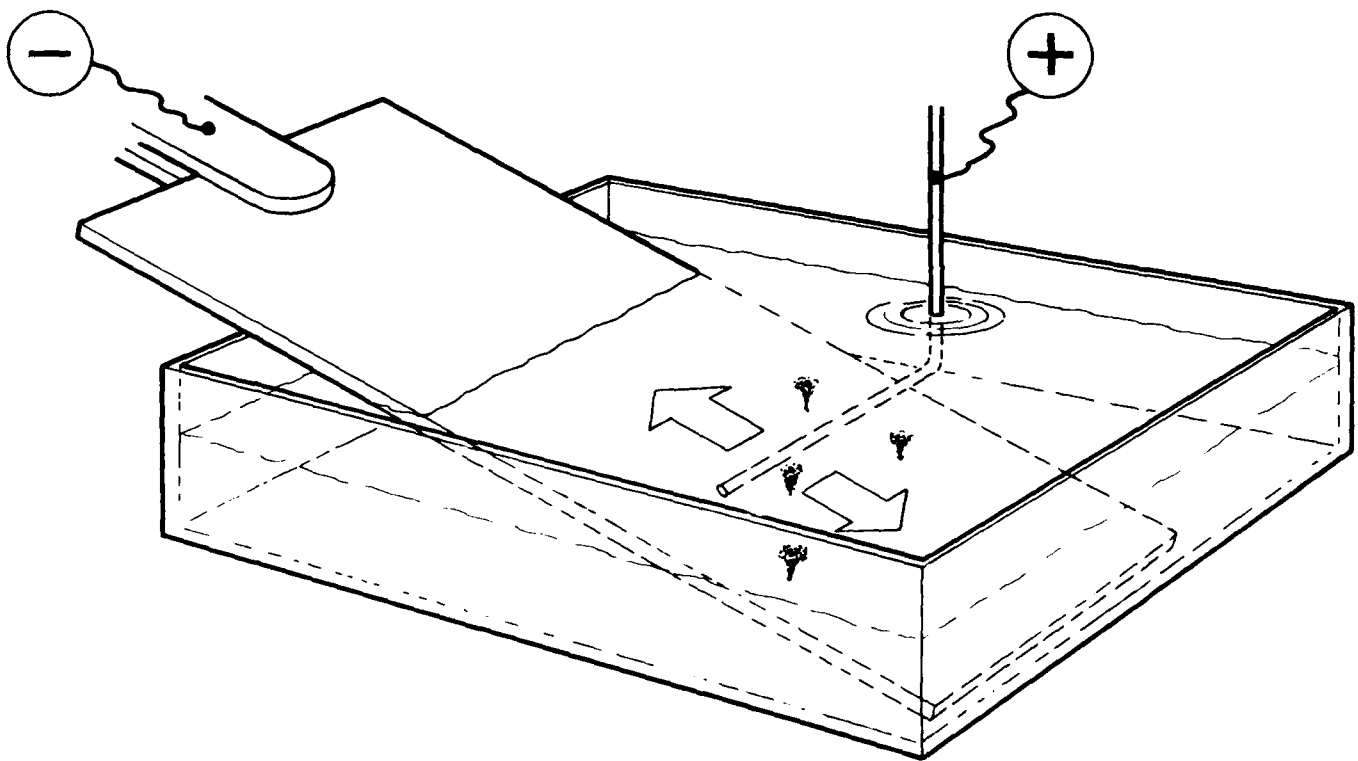
Figure 4-6. Leakage Test

4-70

The test voltage is purposely kept low to avoid any likelihood of dielectric breakdown. For the tests performed in this report, ordinary lantern batteries of 6- or 12-volt DC EMF were used, but lower voltages can be used if desired.

The leak test sensitivity/utility can be adjusted by close attention to the ionic content of the aqueous test cell. Water, in its pure form, is only slightly ionized and as such, equation (1) does not occur to any useful degree. The resistance of pure water is given to be 25 million ohms; therefore, according to Faraday's Law, very little hydroxyl ion will be generated per unit of time at the low voltages used. Generally, laboratory water supplies are quite pure and have resistance of 500,000 ohms or greater. Such high resistance can be unsatisfactory for this test. Very good results are possible by mixing equal volumes of tap water and deionized/distilled water. The slight-to-moderate conductivity that was obtained permits the anode to be used as a wand which is passed over the surface being examined. This permits the surface to be examined incrementally and facilitates examination for the leakage sites under low-power magnification. Increasing the conductivity of the solution significantly, by the addition of acid or salt, results in leakage indications from all leakage sites simultaneously, the instant the voltage is applied. This can be too much to manage if everything turns red suddenly. Finally, further control of the leakage test is possible by varying the voltage used.

4.3.6   LEAKAGE ASSESSMENT -- Of the numerous panels examined for leakage, only a few were found to be nonporous. Porosity was most prevalent in the thinner primer coatings (less than 0.1 mil). As the coating thickness increased, porosity decreased rapidly. Porosity was more often found in localized areas in thick coatings; whereas it was more widespread in some of the thinner coatings. In the less porous coatings, notably the thicker coatings, porosity was generally 3-4 sites per square inch, measuring 3-4 thousandths of an inch in diameter. These are easily overlooked (without the leakage test) because of the transparent nature of the cured primer coating and the low probability

that a void would be found at any one time in the small field of view seen at moderate magnification.

The cause of porosity has not been determined. It is evident, however, that an overall porous condition exists prior to cure of the primer. The porosity seen prior to cure is probably due to evolution of gas at the cathode surface. Other than the superficial craters occupied by gas bubbles at the surface, the connecting porosity to the substrate is quite small and is one magnitude less in size than the porosity seen after cure. Since most of the gas vent porosity seems to disappear during cure, it is possible that the gas vents may provide nucleation for the significantly larger voids seen after cure. Another possibility is that porosity is caused by independent surface tension (wetting) characteristics of the resin in the primer formulation.

Most of the photomicrographs seem to indicate that some sort of surface tension effect occurs during cure wherein the primer either does not wet and flow as well as it might or that the surface can become somewhat phobic to the primer. The experiment with the non-PAA-treated surface discussed in Appendix F seems to indicate that the primer has marginal wetting characteristics during the melt and flow stage of cure. Also, the PAA improves primer adhesion and wetting to the substrate. In this case, state-of-the-art PAA may not fall at times within the wettability envelope requirements of the currently formulated primer.

4.3.7   CONCLUSIONS -- Variations in primer thickness, both across the substrate surface and in total primer film thickness, were the principal cause for adverse results which occurred during the various primer electrodeposition trials. Primer thickness was reported to reduce adhesive bond strength performance when it exceeded 0.00015-inch maximum thickness and, in some instances, we saw evidence of failure occurring in the thick primer layer. At times, we exceeded the maximum allowable primer thickness value by a factor of two and sometimes three times. There was also some evidence of possible adhesive/primer incompatibility in unexplained low lap shear strength values for RB-398 adhesive bonds at 350°F. Further testing would be required in order to explain this anomaly.

The question of primer thickness and uniformity was initially attributed to potential deficiencies in the electrodeposition equipment. Rohr spent considerable time and effort correcting potential deficiencies as they became suspect. At the conclusion of the facility improvement effort, we produced electrodeposited coatings which were identical to those produced concurrently by 3M using a simulated laboratory electrodeposition cell. The primer films produced were barely within nominal-to-maximum thickness range and would have exceeded maximum thickness tolerance with only a second or two additional priming time.

In achieving the required primer thickness of 0.0001-inch nominal, 0.00015-inch maximum, we discovered that the resulting primer films were highly porous but that porosity decreased as the primer film increased in thickness. Our analysis of the porosity condition indicated that a marginal surface tension condition can exist during the primer cure wherein the primer can "fish-eye" on a microscopic scale with very thin primer films, but that this condition is less pronounced as the primer films become thicker. We examined a number of panels which were primed at various times during the program, both at 3M and at Rohr, and found virtually all of them to be porous to some degree.

5/ CONCLUSIONS AND RECOMMENDATIONS

5.1 ELECTRODEPOSITED PRIMER

A number of issues developed during the program which prevented the
scale-up and qualification of the electrodeposited primer system
according to the original program plan. Rohr found it necessary to
deviate from the major program effort of qualifying an electrodeposited
primer and to conduct a more in-depth trial of the process equipment than
originally envisioned. We found, after considerable facility improvement
effort, that the previous Air Force work with respect to the
electrodeposited primer facility design was not applicable to the
electrodeposited primer system optimized under this program. Excellent
strength properties with the desired failure criteria were developed
during Phase I, Task I, in the laboratory but failed to follow suit when
Rohr scaled up to the first level of process equipment design. We
concluded that the current primer formulation needs to be reworked to be
adapted successfully to the current Lockheed facility design.
Alternatively, new process equipment design tailored for the
electrodeposited primer optimized for this program should be considered.

Most of our effort was in response to achieving the required primer
thickness tolerance of 0.0001-inch nominal, 0.00015-inch maximum. We
found that a number of factors could affect our ability to meet the
thickness criteria. Likewise, we found it difficult to remain within the
thickness tolerance once the process parameters had been determined.
Part of the performance inconsistency may disappear upon scale-up to a
larger facility where primer makeup (solvent content, etc.) would not

be as variable. We feel, however, that this benefit may be offset by the more variable electrical conditions present in larger tanks, such as electrode size/shape and distance interrelationships and the effect on uniformity of the primer coating. We did not find the primer optimized in the program to be thickness self-limiting within the thickness tolerance; rather, it could easily exceed the maximum thickness tolerance by a factor of four and was usually 50 percent or greater in thickness at the edge than in the center of the panel.

Adhesive bond strength can be critically affected by the characteristics of the primer interface. In order to achieve the program objectives of 325/350°F performance, we have used polymer materials which are inherently rigid in order to retain sufficient strength properties at elevated temperature. Unfortunately, it is this same rigidity characteristic that can be detrimental tc adhesive bond strength when the primer becomes too thick.

A thin primer film, determined by 3M test to be a requirement to meet program objectives, has shown another condition which was not observed during the Phase I, Task I, primer optimization work. Rohr found, during work with the various process parameters affecting primer thickness, that the primer film was porous, especially in the thinner films required to meet the thickness tolerance requirements. As the primer film was applied thicker, unfortunately exceeding the maximum thickness allowable, the porosity decreased significantly, but often did not completely disappear. Porosity is a direct challenge to the basic corrosion resistance of the primer film because it constitutes a defect through which the substrate is immediately vulnerable to attack. Usually, no immediate corrosive attack is evident because of the protection afforded by the corrosion inhibiting pigments incorporated into the primer; however, the effect of these pigments is finite in that they provide protection by slow dissolution and the release of chemically active agents. The primer successfully passed 30 days of exposure to salt fog (ASTM-B117) without any significant corrosion in Phase I, Task I, testing. This well demonstrates the level of corrosion resistance incorporated into the primer formulation by showing its ability to cope

with a breached film condition in the form of cross-scribes, in addition to probable film porosity. In the long term, however, corrosion resistance will not be of the quality it could have been without the porous film condition. The promise of a void-free coating, envisioned as one of the hallmarks of electrodeposited coatings, did not materialize.

Rohr has found that the various chemical corrosion inhibitors incorporated into adhesive primers will not maintain full corrosion protection for periods much longer than 30 days of salt fog exposure when applied in the low end of the industry-recommended thickness range of 0.0002-inch. Full corrosion resistance, however, can be maintained beyond the 90 days of salt fog exposure when the primer thickness is tripled.

Other significant factors noted during the electrodeposition primer phase of the program were the requirements for maintaining the primer bath. These were: (1) periodic addition of lactic acid to maintain pH and to keep the resin from agglomerating; (2) periodic dialysis to remove ionic species (dissolved corrosion resistant pigment); and (3) periodic addition of solvents. The dialysis requirement represents need for development work and a substantial investment in equipment which must be considered in the economics of electrodeposition priming. Fortunately, chromates are not used in the corrosion resistant pigment composition and as such, waste removal is not as great an issue as it could be. Some localities may require ion exchange treatment of the dialyte. The solvent issue may require more consideration than maintaining the proper solvent concentration in the tank. When the priming tank is in use and left uncovered, solvent freely and quickly leaves the primer bath, facilitated by the rapid flow rate used to keep the bath agitated. For a large priming facility, a significant amount of solvent could be expelled each day. In environmentally sensitive areas, it is probable that some type of air-lock enclosure and solvent-recovery system would be required over the priming tank.

In the final analysis, the electrodeposited primer optimized during the program functionally met program strength objectives only in very thin film thicknesses. This jeopardized our chance of achieving a nonporous

film with the best corrosion resistance performance. We recommend,
therefore, that the primer be further optimized in conjunction with
primer modifications to achieve better processibility and be further
optimized to be fully functional at a greater film thickness. The
electrodeposited primer films reported in AFWAL-TR-87-4087 were nominally
0.0003-inch thick.

Process development work must also center on the instability of XA-3995.
In the laboratory, all of the physical characteristics of XA-3995 meet
the standards set by the program for this material. The objective of
future programs should be to determine the parameters which destabilize
XA-3995 in a production scale-up environment. If necessary, equipment
should be generated which handles XA-3995 properly, or XA-3995 should be
reformulated to make it one step more stable. If equipment design cannot
solve the problem, the problem may be the stabilization system for the
particulates in XA-3995. Presently, the dispersing aid is the base
polymer itself. The patent literature indicates that the synthesis and
utilization of dispersing aids designed for specific systems may be of
use in stabilizing particulate dispersion in CEDSABPs. (See Section 6,
Item 6.) Regarding equipment design, suppliers of electrophoretic
deposition equipment to the automotive industry may be of service. We
found them to be very helpful in determining the requirements for
industrial size ultra-filtration equipment in our Phase II scale-up
study.

5.2   WATER-BASE PRIMER

The water-base primer materials tested under the program performed very
well considering their relative newness to the aircraft industry. Two of
the materials tested had just emerged from the development laboratory
and had not received any in-depth refinement. Product refinement usually
results when a material supplier/manufacturer interface is formed to
qualify a material for production use. For production applications,
specific end-use criteria are established for the product which are
vigorously pursued. We feel that this level of effort and motivation
will be required to bring water-base primers to a competitive position
with current solvent-base adhesive bonding primers.

Environmental impact issues such as air pollution and toxic waste disposal promise to motivate continued industry interest in water-base primers. At Rohr, we are looking very strongly at water-base primers for our own product lines. We are also seeking customer support for the use of water-base primers on subcontracted assemblies.

Although a best primer was selected for Phase I, Task III testing, the program also identified two other water-base primers which were capable of meeting military specification requirements for adhesive bonding. The primers were each from different major aerospace adhesive manufacturers. This is gratifying as it means that a majority of the aerospace adhesive suppliers are now working with water-base primers. Each manufacturer is a potential source for adhesive systems packaged with an optimized water-base primer.

Finally, the chromated paint primer tested on the program should be tested further for possible use for moderate temperature service adhesive bond repairs. This type of material is usually present in maintenance areas and could be used effectively with the "patch kits" typically employed. The corrosion resistance of the paint primer was noticeably better than the other water-base primers tested. We feel that the corrosion resistance performance of the adhesive primers needs to be improved to the same level as the paint primer.

6/ REFERENCES

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5. D.A. Ansdell, in "Paint and Surface Coatings: Theory and Practice," R. Lambourne, ed., Ellis Horwood Ltd., Chichester, UK, 1987, pp. 446-448.

6. See U.S. Patent 4,579,889, U.S. Patent 4,608,139.

Performance Parameter

Bell Peel Strength

	RT	
	4	CP
	4	CP
Avg.	4	

Lap Shear Strength

	-67F		RT		325F		350F	
	3159	CA/CP	3288	CA/CP	3253	CA	3269	CA
	3393	CA/CP	3670	CA/CP	3380	CA	3198	CA
	3650	CA/CP	3544	CA/CP	3182	CA	3101	CA
Avg.	3400.666	Avg.	3500.666	Avg.	3271.666	Avg.	3189.333	
Max. Ind.	3650	Max. Ind.	3670	Max. Ind.	3380	Max. Ind.	3269	
Min. Ind.	3159	Min. Ind.	3288	Min. Ind.	3182	Min. Ind.	3101	

Lap Shear Strength After 200 Hours at 350 F

		325F	
		3600	CA
		3540	CA
		3300	CA
	Avg.	3480	
	Max. Ind.	3600	
	Min. Ind.	3300	

Flatwise Tension

	RT		325F	
	750	CA	385	CA
	688	CA	403	CA
Avg.	719	Avg.	394	

"Facial" Corrosion
Scribed Panel
30 Days Salt Spray Exposure

GENERAL CORROSION OVER 60% OF PANEL
SURFACES. COATING WAS SUBVERTED
COMPLETELY IN UPPER 50% OF PANEL

Lap Shear Strength
After 30 Days
Salt Spray Exposure

		RT		
		3940	CA/CP	No Bondline Corrosion
		3938	CA/CP	No Bondline Corrosion
		3938	CA/CP	No Bondline Corrosion
	Avg.	3938.666		
	Max. Ind.	3940		
	Min. Ind.	3938		

Lap Shear Bonds
on Titanium

	-67F		RT		325F		350F	
	2973	APM	4093 2	CA/CP	3523	CA	3279	CA
	3023	APM	3694	CA/CP	3499	CA	3204	CA
	2611	APM	3931	CA/CP	3177	CA	3076	CA
Avg.	2869 Avg.		3906.066 Avg.		3399.666 Avg.		3186.333	

Lap Shear Bonds
on Titanium
After 200 Hours
at 350F

		325F	
		3890	CA
		3600	CA
		3600	CA
	Avg.	3696.666	

Table A-2.   CEDSABP Optimization Program, CEDSABP No. 1

Performance Parameter

Deposition Characteristics at	(1/e) value	Throwpower Excellent. coating is just slightly rough, costs HC core full depth
10V	1.6 sec	
20V	0.6 sec	
30V	0.6 sec	
40V	1.0 sec	
50V	1.2 sec	
60V	1.6 sec	

Film Properties at	Thickness	Hardness
10v	0.069	9H
20V	0.09	9H
30V	0.12	9H
40V	0.22	9H
50V	0.25	9H
60V	0.29	9H

Bell Peel Strength

	RT	
	5	CA
	6	CA
Avg.	5.5	

Lap Shear Strength

	-67F		RT		325F		350F	
	4480	CA/CP	3606	CA	3380	CA	3150	CA
	3820	CA/CP	3978	CA	3450	CA	3320	CA
	3820	CA/CP	3522	CA	3280	CA	3080	CA
Avg.	4040	Avg.	3702	Avg.	3370	Avg.	3183.333	
Max. Ind.	4480	Max. Ind.	3978	Max. Ind.	3450	Max. Ind.	3320	
Min. Ind.	3820	Min. Ind.	3522	Min. Ind.	3280	Min. Ind.	3020	

Lap Shear Strength
After 200 Hours
at 350 F

	325F	
	3890	CA
	3820	CA
	3860	CA
Avg.	3856.666	
Max. Ind.	3890	
Min. Ind.	3820	

Flatwise Tension

	RT		325F	
	777.5	CA	456.2	CA
	687.5	CA	462.5	CA
Avg.	732.5	Avg.	459.35	

"Facial" Corrosion · No Blistering · Visible Drip Marks
Scribed Panel · No Peeling · Small Blisters in Scribe
30 Days Salt Spray Exposure · No Creep from Scribe

Lap Shear Strength
After 30 Days
Salt Spray Exposure

	RT		
	4470	CA	No Bondline Corrosion
	4352	CA	No Bondline Corrosion
	4542	CA	No Bondline Corrosion
Avg.	4454.666		
Max. Ind.	4542		
Min. Ind.	4352		

Lap Shear Bonds on Titanium		-67F		RT		325F		350F	
		3000	APM	3824	CA	3500	CA	3020	CA
		5000	APM	4004	CA/APM	3600	CA	3320	CA
		4080	APM	4296	CA/APM	3650	CA	3360	CA
	Avg.	4026.666	Avg.	4041.333	Avg.	3583.333	Avg.	3233.333	

Lap Shear Bonds on Titanium After 200 Hours at 350F			325F	
			4220	CA
			4200	CA
			4060	CA
		Avg.	4160	

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at	(1/e) value	Throwpower Very good. Same roughness as at 0 days. Completely coats core at 40V.
10V	3.8 sec	Coating is yellower than at 0 days.
20V	0.9 sec	
30V	0.6 sec	
40V	0.4 sec	
50V	0.5 sec	
60V	0.7 sec	

Film Properties at	Thickness	Hardness
10v	0.06	8H
20V	0.155	9H
30V	0.24	9H
40V	0.29	9H
50V	0.29	9H
60V	0.29	9H

Lap Shear Strength After 200 Hours at 350 F 2024-T81		325F	
		3300	CA
		3280	CA
		3280	CA
	Avg.	3286.666	
	Max. Ind.	3300	
	Min. Ind.	3280	

Lap Shear Strength After 200 Hours at 350 F Titanium		325F	
		3140	CA
		3360	CA
		3250	CA
	Avg.	3250	
	Max. Ind.	3360	
	Min. Ind.	3140	

Table A-3. CEDSABP Optimization Program, CEDSABP No. 2

Performance Parameter

Deposition Characteristics at	(1/e) value	Throwpower excellent, Semi-Gloss Coating, Coats HC core completely
10V	2.4 sec	
20V	0.6 sec	
30V	0.8 sec	
40V	0.6 sec	
50V	0.8 sec	
60V	0.6 sec	

Film Properties at	Thickness	Hardness
10V	0.128	9H
20V	0.174	9H
30V	IRR	
40V	IRR	
50V	IRR	
60V	IRR	

Bell Peel Strength	RT	
	4	CA
	4	APM
	6	CA
	6	APM
Avg.	5	

Lap Shear Strength	-67F		RT		325F		350F	
	3980	CA/CP	3950	CA/CP	3400	CA	3120	CA
	4500	CA/CP	4004	CA	3420	CA	3000	CA
	4500	CA/CP	3944	CA	3480	CA	3150	CA
Avg.	4326.6666		3966		3433.333		3090	
Max. Ind.	4500		4004		3480		3150	
Min. Ind.	3980		3944		3400		3000	

Lap Shear Strength After 200 Hours at 350 F		325F	
		3980	CA
		3820	CA
		3900	CA
	Avg.	3900	
	Max. Ind.	3980	
	Min. Ind.	3820	

Flatwise Tension		RT		325F		
		687.5	CA/CP	500	CA	*Core Failure
		690	CA/CP	485	CA	
		752.5 *		Avg.	492.5	
	Avg.	710				

Scribed "Facial" Panels 30 Day Salt Spray	No Blistering	Visible drip marks
	No Peeling	Small blisters in scribes
	No creep from scribe	

Table A-3. CEDSABP Optimization Program, CEDSABP No. 2 (Cont.)

Lap Shear Strength		RT		
After 30 Days		4578	CA	No Bondline Corrosion
Salt Spray Exposure		4106	CA	No Bondline Corrosion
		4872	CA	No Bondline Corrosion
	Avg.	4518.666		
	Max. Ind.	4872		
	Min. Ind.	4106		

Lap Shear Bonds		-67F		RT		325F		350F	
on Titanium		4980	APM	3770	CA	3550	CA/CP	3400	CA/CP
		5280	APM	3134	APM	3420	CA/CP	3080	CA/CP
	Avg.	5130	Avg.	3452	Avg.	3485	Avg.	3240	

Lap Shear Bonds		325F	
on Titanium		3380	CA/CP
After 200 Hours		3440	CA/CP
at 350F	Avg.	3410	

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at	(1/e) value	Throwpower excellent. Semi Gloss Coating,
10V	2.3 sec	Coats HC core completely.
20V	0.75 sec	At higher V., coating becomes spotted.
30V	0.5 sec	
40V	0.4 sec	
50V	0.6 sec	
60V	0.5 sec	

Film Properties at	Thickness	Hardness
10v	0.04	9H
20V	0.08	9H
30V	0.1	9H
40V	0.14	9H
50V	0.15	9H
60V	0.17	9H

Lap Shear Strength		RT	
psi		3762	CA
		3722	CA
		4120	CA
	Avg.	3868	

Lap Shear Strength		325F	
After 200 Hours		3920	CA
at 350 F		3840	CA
On 2024-T81 Aluminum		3980	CA
	Avg.	3913.333	
	Max. Ind.	3980	
	Min. Ind.	3840	

Lap Shear Strength		325F	
After 200 Hours		3750	CA
at 350F		3780	CA
on Titanium		3720	CA
	Avg.	3750	
	Max. Ind.	3780	

Performance Parameter

Deposition Characteristics at	(1/e) value		Throwpower excellent. Completely coats core.
10V	2.6 sec		Semi-gloss continuous coating.
20V	1.3 sec		
30V	0.7 sec		
40V	0.5 sec		
50V	0.5 sec		
60V	0.3 sec		

Film Properties at	Thickness	Hardness
10v	0.034	9H
20V	0.108	9H
30V	0.104	9H
40V	0.124	9H
50V	0.136	9H
60V	0.142	9H

Bell Peel Strength

	RT	
	6	CA
	6	CA
Avg.	6	

Lap Shear Strength

	-67F		RT		325F		350F	
	4000	CA/CP	3643	CA	3384	CA	3246	CA
	3498	CA/CP	3539	CA	3390	CA	3080	CA
	4084	CA/CP	3538	CA	3387	CA	2990	CA
Avg.	3860.6666	Avg.	3573.333	Avg.	3387	Avg.	3105.333	
Max. Ind.	4084	Max. Ind.	3643	Max. Ind.	3390	Max. Ind.	3246	
Min. Ind.	3498	Min. Ind.	3538	Min. Ind.	3384	Min. Ind.	2990	

Lap Shear Strength
After 200 Hours
at 350 F

		325F	
		3420	CA
		3400	CA
		3320	CA
	Avg.	3380	
	Max. Ind.	3420	
	Min. Ind.	3320	

Flatwise Tension

	RT		325F		
	610	CA	463	CA	
	715*	CA	500	CA	*Some core failure
Avg.	662.5	Avg.	481.5		

Scribed "Facial" Panels	No Blistering	Some drip marks.
30 Day Salt Spray	No Peeling	Small (few) blisters in scribe.
	No Crep from Scribes	

Lap Shear Strength
After 30 Days
Salt Spray Exposure

	RT		
	4238	CA	No Bondline Corrosion
	4134	CA	No Bondline Corrosion
	4134	CA	No Bondline Corrosion
Avg.	4168.666		
Max. Ind.	4238		
Min. Ind.	4134		

Table A-4. CEDSABP Optimization Program, CEDSABP No. 2 Replicate (Cont.)

Lap Shear Bonds on Titanium		-67F		RT		325F		350F	
		3580	AP/CP	4788	AP/CP/CA	3360	CA	3060	CA
		4400	AP/CP	3754	AP/CP/CA	3280	CA	2920	CA
		4280	AP/CP	3728	AP/CP/CA	3250	CA	3130	CA
	Avg.	4086.6666	Avg.	4090	Avg.	3296.666	Avg.	3036.666	

Lap Shear Bonds on Titanium After 200 Hours at 350F		325F	
		3640	CA
		3620	CA
		3440	CA
	Avg.	3566.666	

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at	(1/e) value	
10V	19.0 sec	Throwpower moderate.Coats core only about 1/8".
20V	2.5 sec	Somewhat rough coating at higher V.
30V	1.8 sec	
40V	1.4 sec	
50V	0.9 sec	
60V	0.8 sec	

Film Properties at	Thickness	Hardness
10v	0.04 mils	8H
20V	0.133 mils	9H
30V	0.21 mils	9H
40V	0.29 mils	9H
50V	0.25 mils	9H
60V	0.26 mils	9H

Lap Shear Strength After 200 Hours at 350 F On 2024-T81 Aluminum		325F
		3440
		3420
		3480
	Avg.	3446.666
	Max. Ind.	3480
	Min. Ind.	3420

Lap Shear Strength After 200 Hours at 350F on Titanium		325F
		3080
		3240
		3600
	Avg.	3306.666
	Max. Ind.	3600
	Min. Ind.	3080

Table A-5. CEDSABP Optimization Program, CEDSABP No. 2
Second Replicate

Performance Parameter

Deposition Characteristics at	(1/e) value	Throwpower excellent. Uniform coating.
10V	10.0 sec	Coats core completely @ 20V.
20V	2.0 sec	
30V	1.5 sec	
40V	0.9 sec	
50V	0.0 sec	
60V	0.8 sec	

Film Properties at	Thickness	Hardness
10v	-	-
20V	0.17 mils	9H
30V	0.19 mils	9H
40V	0.24 mils	9H
50V	0.18 mils	9H
60V	0.18 mils	9H

Bell Peel Strength	RT	
	5	CA
	6	CA
	5	CA
	6	CA
Avg.	5.5	

Lap Shear Strength	-67F		RT		325F		350F	
	3750	CA/CP	3850	CA	3720	CA	3050	CA
	3920	CA/CP	3480	CA	3160	CA	3080	CA
	3700	CA/CP	3550	CA	3480	CA	3220	CA
Avg.	3790	Avg.	3627	Avg.	3453	Avg.	3117	
Max. Ind.	3920	Max. Ind.	3850	Max. Ind.	3720	Max. Ind.	3220	
Min. Ind.	3700	Min. Ind.	3480	Min. Ind.	3160	Min. Ind.	3050	

Lap Shear Strength After 200 Hours at 350 F		325F	
		3800	CA
		3700	CA
		3800	CA
	Avg.	3767	
	Max. Ind.	3800	
	Min. Ind.	3700	

Flatwise Tension		RT		325F		
		781	CA	444	CA	
		800	CA	435	CA	*Some core failure
	Avg.	791	Avg.	439		

Scribed "Facial" Panels 30 Day Salt Spray	Some General Corrosion	No peeling
	Pits	No blistering
	Blisters in Scribes	

Lap Shear Strength After 30 Days Salt Spray Exposure		RT		
		4376	CA	No Bondline Corrosion
		4786	CA	No Bondline Corrosion
		4418	CA	No Bondline Corrosion
	Avg.	4527		
	Max. Ind.	4786		
	Min. Ind.	4376		

Table A-5. CEDSABP Optimization Program, CEDSABP No. 2
Second Replicate (Cont.)

Lap Shear Bonds		-67F		RT		325F		350F	
on Titanium		3740	CA/CP/APM	4450	CA/CP	3650	CA	3150	CA
		3900	CA/CP/APM	4280	CA/CP	3780	CA	3300	CA
		3980	CA/CP/APM	4450	CA/CP	3650	CA	3500	CA
	Avg.	3873	Avg.	4393	Avg.	3693	Avg.	3317	

Lap Shear Bonds		325F	
on Titanium		3850	CA
After 200 Hours		3880	CA
at 350F		4020	CA
	Avg.	3917	

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at	(1/e) value
10V	>40 sec
20V	>40 sec
30V	>40 sec
40V	>40 sec
50V	>40 sec
60V	>40 sec

At 30V, most of cell is coated, thicker at edges, patterned.

Film Properties at	Thickness	Hardness
10B	0.1 mils	9H
20V	0.12 mils	9H
30V	No coat	
40V	No coat	
50V	No coat	
60V	No coat	

Lap Shear Strength		325F
After 200 Hours		3660
at 350 F		3760
On 2024-T81 Aluminum		3440
	Avg.	3620
	Max. Ind.	3760
	Min. Ind.	3440

Lap Shear Strength		325F
After 200 Hours		3580
at 350F		3700
on Titanium		3560
	Avg.	3613
	Max. Ind.	3700

Table A-6. CEDSABP Optimization Program, CEDSABP No. 3

Performance Parameter

Deposition Characteristics at	(1/e) value	
10V	16.5 sec	Throwpower tends to be thick on edges, thin in middle.
20V	7.0 sec	Lumpy coating when thick. Coats honeycomb edges only.
30V	4.8 sec	
40V	4.0 sec	
50V	2.9 sec	
60V	2.3 sec	

Film Properties at	Thickness	Hardness
10V	-	-
20V	0.4	9H
30V	0.13	9H
40V	0.17	9H
50V	1.13	9H
60V	1.05	9H

Bell Peel Strength	RT
	6
	5
Avg.	5.5

Lap Shear Strength	-67F		RT		325F		350F	
	3025	CP	2852	CA	2358	CA	2083	CA
	2668	CP	2748	CA	2608	CA	2192	CA
	2876	CP	2609	CA	2808	CA	2452	CA
Avg.	2856.3333	Avg.	2736.333	Avg.	2591.333	Avg.	2242.333	
Max. Ind.	3025	Max. Ind.	2852	Max. Ind.	2808	Max. Ind.	2452	
Min. Ind.	2668	Min. Ind.	2609	Min. Ind.	2358	Min. Ind.	2083	

Lap Shear Strength After 200 Hours at 350 F	325F	
	3200	CA
	3200	CA
	3400	CA
Avg.	3266.666	
Max. Ind.	3400	
Min. Ind.	3200	

Flatwise Tension	RT		325F	
	769	CA	444	CA
	800	CA	435	CA
Avg.	784.5	Avg.	439.5	

Scribed "Facial" Panels 30 Day Salt Spray

Lap Shear Strength After 30 Days Salt Spray Exposure	RT		
	3540	CA/CP	No Bondline Corrosion
	3414	CA/CP	No Bondline Corrosior
	3330	CA/CP	No Bondline Corrosion
Avg.	3428		
Max. Ind.	3540		
Min. Ind.	3330		

Lap Shear Bonds on Titanium		-67F		RT		325F		350F	
		2084	CA/CP	2552	AP/CP	2203	AP/CA	2186	AP/CA
		1766	AP/CP	2751	AP/CP	2361	AP/CA	1981	AP/CA
		2355	AP/CP	2398	AP/CP	2219	AP/CA	1942	AP/CA
	Avg.	2068.3333	Avg.	2555	Avg.	2261	Avg.	2036.333	

Adhesion failure
seems to occur
on thick coating

Lap Shear Bonds on Titanium After 200 Hours at 350F		325F	
		2480	CA
		2600	CA
		2620	CA
	Avg.	2566.666	

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at (1/e) value		Throwpower poor. Lumpy rough coating.
10V	>40 sec	Coats HC core edges only.
20V	>40 sec	
30V	>40 sec	
40V	>40 sec	
50V	>40 sec	
60V	>40 sec	

Film Properties at	Thickness	Hardness
10V	0.35 mils	9H
20V	0.35 mils	9H
30V	0.35 mils	9H
40V	0.35 mils	9H
50V	0.35 mils	9H
60V	0.35 mils	9H

Lap Shear Strength After 200 Hours at 350 F On 2024-T81 Aluminum		325F
		3300
		3320
		3220
	Avg.	3280
	Max. Ind.	3320
	Min. Ind.	3220

Lap Shear Strength After 200 Hours at 350F on Titanium		325F
		3400
		3600
		3500
	Avg.	3500
	Max. Ind.	3600
	Min. Ind.	3600

Performance Parameter

Deposition Characteristics at (1/e) value		Throwpower Fair to Good. Glossy Coating.
10V	>40 sec	Tends to be Thick on Flat Plate Edges.
20V	3.5 sec	Coats HC core edges only
30V	1.75 sec	
40V	1.3 sec	
50V	0.8 sec	
60V		

Film Properties at	Thickness	Hardness
10v	-	
20V	-	
30V	0.13	9H
40V	0.41	9H
50V	0.42	
60V	0.48	

Bell Peel Strength

	RT	
	6	CA/CP
	6	CA
Avg.	6	

Lap Shear Strength

	-67F		RT		325F		350F	
	3720	CP	3654	CA/CP	3440	CA	2940	CA
	3820	CP	3050	CA/CP	3200	CA	3120	CA
	3930	CP	3620	CA/CP	3240	CA	2920	CA
Avg.	3823.333	Avg.	3441.333	Avg.	3293.333	Avg.	2993.333	
Max. Ind.	3930	Max. Ind.	3654	Max. Ind.	3440	Max. Ind.	3120	
Min. Ind.	3720	Min. Ind.	3050	Min. Ind.	3200	Min. Ind.	2920	

Lap Shear Strength After 200 Hours at 350 F

	325F	
	3400	CA
	3360	CA
	3500	CA
Avg.	3420	
Max. Ind.	3500	
Min. Ind.	3360	

Flatwise Tension

	RT		325F	
	750	CA	437.5	CA
	697.5	CA	437.5	CA
Avg.	723.75	Avg.	437.5	

"Facial" Scribed Panel 30 Days Salt Spray Exposure

No Blisters   No Drip Marks
No Creep From Scribe
No Peeling

Lap Shear Strength After 30 Days Salt Spray Exposure

	RT		
	3764	CP	No Bondline Corrosion.
	3550	CP	No Bondline Corrosion.
	3724	CP	No Bondline Corrosion.
Avg.	3679.333		
Max. Ind.	3764		
Min. Ind.	3550		

Lap Shear Bonds on Titanium		-67F		RT		325F		350F	
		3160	APM	4260	APM	3050	CA	2760	CA
		3000	APM	3426	APM	3040	CA	2480	CA
		3240	APM	3338	APM	2620	CA	2560	CA
	Avg.	3133.333	Avg.	3674.666	Avg.	2903.333	Avg.	2600	

Lap Shear Bonds on Titanium After 200 Hours at 350F		325F	
		3320	CA/CP
		3380	CA/CP
		3360	CA/CP
	Avg.	3353.333	

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at (1/e) value		Throwpower Poor. Lumpy coating.
10V	>40 sec	Coats HC core 1/8" into cell
20V	>40 sec	
30V	>40 sec	
40V	>40 sec	
50V	>40 sec	
60V	>40 sec	

Film Properties at	Thickness	Hardness
at		
10v	0.1	9H
20V	0.35	9H
30V	0.57	9H
40V	0.17	9H
50V	0.26	9H
60V	0.25	9H

Lap Shear Strength After 200 Hours at 350 F On Aluminum		325F	
		3680	CA
		3940	CA
		3580	CA
	Avg.	3733.333	
	Max. Ind.	3940	
	Min. Ind.	3580	

Lap Shear Strength After 200 Hours at 350 F On Titanium		325F		
		3380	CA	Somewhat lumpy
		3700	CA	coating.
		3540	CA	
	Avg.	3540		
	Max. Ind.	3700		
	Min. Ind.	3380		

Table A-8. CEDSABP Optimization Program, CEDSABP No. 5

Performance Parameter

Deposition Characteristics at (1/e) value		Throwpower Excellent
10V	2.2 sec	
20V	0.8 sec	
30V	0.9 sec	
40V	0.7 sec	
50V	0.6 sec	
60V	0.7 sec	

Film Properties at	Thickness	Hardness
10v	0.06	9H
20V	0.13	9H
30V	0.14	9H
40V	0.2	9H
50V	0.28	9H
60V	0.29	9H

Bell Peel Strength

	RT	
	4	CA
	4	CA
Avg.	4	

Lap Shear Strength

	-67F		RT		325F		350F	
	3580	CA/CP	3402	CA	3500	CA	3280	CA
	3900	CA/CP	3322	CA	3540	CA	2500	CA
	4100	CA/CP	3452	CA	3640	CA	3400	CA
Avg.	3860	Avg.	3392	Avg.	3560	Avg.	3060	
Max. Ind.	4100	Max. Ind.	3452	Max. Ind.	3640	Max. Ind.	3400	
Min. Ind.	3580	Min. Ind.	3322	Min. Ind.	3500	Min. Ind.	2500	

Lap Shear Strength
After 200 Hours
at 350 F

	325F	
	3960	CA
	3960	CA
	3650	CA
Avg.	3856.666	
Max. Ind.	3960	
Min. Ind.	3650	

Flatwise Tension

	RT		325F	
	781.2	CA	472.2	CA
	797.5	CA	487.5	CA
Avg.	789.35	Avg.	479.85	

"Facial" Corrosion — No Blisters — No drip marks
Scribed Panel — No Creep from Scribe
30 Days Salt Spray Exposure — No Peeling.

Lap Shear Strength
After 30 Days
Salt Spray Exposure

	RT		
	4788	CA/CP	No Bondline Corrosion.
	5002	CA/CP	No Bondline Corrosion.
	4634	CA/CP	No Bondline Corrosion.
Avg.	4808		
Max. Ind.	5002		
Min. Ind.	4634		

Table A-8. CEDSABP Optimization Program, CEDSABP No. 5 (Cont.)

Lap Shear Bonds		-67F		RT		325F		350F	
on Titanium		3060	CP	3136	CP	3200	CA/CP	2820	CA/CP
		3980	CP	3560	CP/APM	3440	CA/CP	2880	CA/CP
		4100	APM	3860	CP	2850	CA/CP	2520	CA/CP
	Avg.	3713.333	Avg.	3518.666	Avg.	3163.333	Avg.	2740	

Poor Coating
On Titanium
LUMPY!

Lap Shear Bonds		325F	
on Titanium		3680	CA
After 200 Hours		3750	CA
at 350F		3660	CA
	Avg.	3696.666	

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at	(1/e) value	
10V	6.2 sec	Throwpower Very good Completely coats
20V	0.9 sec	HC core at higher V.
30V	0.5 sec	Coating is slightly rough at high V.
40V	0.5 sec	Coating on Ti is rough.
50V	0.5 sec	
60V	0.4 sec	

Film Properties at	Thickness	Hardness
10v	0.036	8H
20V	0.1	9H
30V	0.28	9H
40V	0.27	9H
50V	0.13	9H
60V	0.18	9H

Lap Shear Strength		325F	
After 200 Hours		3120	
at 350 F		3040	CA
2024-T81		3000	CA
	Avg.	3053.333	CA
	Max. Ind.	3120	
	Min. Ind.	3000	

Lap Shear Strength		325F	
After 200 Hours		3080	
at 350 F		3280	CA
Titanium		3360	CA
	Avg.	3240	CA
	Max. Ind.	3240	
	Min. Ind.	3360	

Table A-9. CEDSABP Optimization Program, CEDSABP No. 6

Performance Parameter

Deposition Characteristics at	(1/e) value	
10V	26.8 sec	Throwpower Excellent.
20V	8 sec	Glossy coating.
30V	4 sec	Coats HC core throughout.
40V	1.8 sec	Somewhat lumpy at high V.
50V	1.8 sec	
60V	1 sec	

Film Properties at	Thickness	Hardness
10v	0.127	9H
20V	0.317	9H
30V	0.265	9H
40V	0.284	9H
50V	IRR	
60V	IRR	

Bell Peel Strength	RT	
	6	CA
	5	CA
	4	CA
	5	CA
Avg.	5	

Lap Shear Strength	-67F		RT		325F		350F	
	4600	CA/CP	3804	CA	3840	CA	3460	CA
	4080	CA/CP	3560	CA	3680	CA	3360	CA
	3500	CA/CP	3506	CA	3960	CA	3540	CA
Avg.	4060	Avg.	3623.333	Avg.	3826.666	Avg.	3453.333	
Max. Ind.	4600	Max. Ind.	3804	Max. Ind.	3960	Max. Ind.	3540	
Min. Ind.	3500	Min. Ind.	3506	Min. Ind.	3680	Min. Ind.	3360	

Lap Shear Strength After 200 Hours at 350 F	325F	
	3800	CA
	3800	CA
	3820	CA
Avg.	3806.666	
Max. Ind.	3820	
Min. Ind.	3800	

Flatwise Tension	RT		325F	
	812.5	CA	485	CA
	812.5	CA	472.5	CA
	715	CA Avg.	478.75	
Avg.	780			

"Facial" Scribed Panel	No Blisters	Slight Drip Marks
30 Day Salt Spray	No Peeling	Small Blisters in Scribe
Exposure	No Creep From Scribe	

Lap Shear Strength		RT			
After 30 Days		4104	CA	No Bondline Corrosion	
Salt Spray Exposure		4846	CA	No Bondline Corrosion	
		4C62	CA	No Bondline Corrosion	
	Avg.	4337.333			
	Max. Ind.	4846			
	Min. Ind.	4062			

Lap Shear Bonds		-67F		RT		325F		350F	
on Titanium		2500	APM	2486	APM	3280	CA/CP	3000	CA/CP
		2900	APM	3124	APM	3000	CA/CP	2750	CA/CP
	Avg.	2700 Avg.		2805 Avg.		3140 Avg.		2875	

Lap Shear Bonds		325F	
on Titanium		3680	CA
After 200 Hours		3380	CA
at 350F	Avg.	3530	

Bath Stability
Physical Properties
After 30 Days
Stirring

Deposition Characteristics at (1/e) value		Throwpower Poor.
10V	>40 sec	Does Not Coat.
20V	>40 sec	
30V	>40 sec	
40V	>40 sec	
5.V	>40 sec	
60V	>40 sec	

Film Properties at	Thickness	Hardness
10v	CEDSABP Agglomerated	
20V		
30V		
40V		
50V		
60V		

Lap Shear Strength		325F
After 200 Hours		Will Not Be Run
at 350 F	Avg.	ERR
	Max. Ind.	ERR
	Min. Ind.	ERR

Table A-10. CEDSABP Optimization Program, CEDSABP No. 7

Performance Parameter

Deposition Characteristics at (1/e) value		
10V	17.0 sec	Throwpower Poor.
20V	5.6 sec	Coats core only 1/16".
30V	3.2 sec	Thick, glossy coating.
40V	2.2 sec	Thick on edges.
50V	2.1 sec	
60V	1.6 sec	

Film Properties at	Thickness	Hardness
10V	-	9H
20V	0.17	9H
30V	0.32	9H
40V	0.72	9H
50V	0.91	9H
60V	0.78	9H

Bell Peel Strength	RT
	5
	5
Avg.	5

Lap Shear Strength	-67F		RT		325F		350F	
	3491	CP/AP	3451	CP/CA	3036	CA	2746	CA
	2914	CP/AP	3472	CP/CA	3300	CA	292˙	CA
	3374	CP/AP	3011	CP/CA	2939	CA	2920	CA
Avg.	3259.6666	Avg.	3311.333	Avg.	3091.666	Avg.	2864	
Max. Ind.	3491	Max. Ind.	3472	Max. Ind.	3300	Max. Ind.	2926	
Min. Ind.	2914	Min. Ind.	3011	Min. Ind.	2939	Min. Ind.	2746	

Lap Shear Strength After 200 Hours at 350 F	325F	
	3380	CA
	3360	CA
	3360	CA
Avg.	3366.666	
Max. Ind.	3380	
Min. Ind.	3360	

Flatwise Tension	RT		325F	
	750	CA	423	CA
	710	CA	472	CA
Avg.	730	Avg.	447.5	

Scribed "Facial" Panels 30 Day Salt Spray	No Flisters	Small (few) blisters in scribe
	No creep from scribe	Possible pits at coating imperfections
	No peeling	

Lap Shear Strength After 30 Days Salt Spray Exposure	RT	
	3712	CA
	3532	CA
	3460	CA
Avg.	3568	
Max. Ind.	3712	
Min. Ind.	3460	

Lap Shear Bonds on Titanium	-67F		RT		325F		350F	
	2861	AP	3497	AP/CP/CA	3172	CA	2423	CA
	2940	AP	3154	AP/CP/CA	3077	CA	2513	CA
	2483	AP	3073	AP/CP/CA	2714	CA	2886	CA
Avg.	2761.3333	Avg.	3241.333	Avg.	2987.666	Avg.	2607.333	

Lap Shear Bonds on Titanium After 200 Hours at 350F	325F	
	3900	CA
	3450	CA
	3300	CA
Avg.	3550	

Bath Stability
Physical Properties
After 30 Days
Stirring

Deposition Characteristics at	(1/e) value	
10V	40 sec	Throwpower Poor.
20V	40 sec	Coats HC core only 1/32".
30V	30.3 sec	Very rough coating at high V.
40V	24.2 sec	
50V	14.4 sec	
60V	10.7 sec	

Film Properties at	Thickness	Hardness
10v	-	
20V	0.2 mils	9H
30V	0.53 mils	9H
40V	0.75 mils	9H
50V	1.04 mils	9H
60V	1.2 mils	9H

Lap Shear Strength After 200 Hours at 350 F On 2024-T81 Aluminum	325F
	3200
	3120
	3160
Avg.	3160
Max. Ind.	3200
Min. Ind.	3120

Lap Shear Strength After 200 Hours at 350F on Titanium	325F
	3060
	3420
	3380
Avg.	3286.666
Max. Ind.	3420
Min. Ind.	3060

Performance Parameter

Deposition Characteristics at	(1/e) value	
10V	9.3 sec	Throwpower Moderate. Slightly thick on edges.
20V	2.8 sec	Coats HC core 1/2 way in.
30V	1.6 sec	Nice glossy coating on flat sheet.
40V	1.3 sec	
50V	0.8 sec	
60V	0.7 sec	

Film Properties at	Thickness	Hardness
10v	-	
20V	0.068	
30V	0.178	9H
40V	0.36	9H
50V	0.41	9H
60V	0.44	9H

Bell Peel Strength

	RT	
	3	CP
	4	CP
	3	CP
	3	CP
Avg.	3.25	

Primer likely too thick.

Lap Shear Strength

	-67F		RT		325F		350F	
	4480	APM/CP	3280	CA/CP	3300	CA	2960	CA
	4200	APM/CP	3400	CA/CP	3120	CA	2820	CA
	4040	APM/CP	3500	CA/CP	3060	CA	2660	CA
Avg.	4240	Avg.	3393.333	Avg.	3160	Avg.	2813.333	
Max. Ind.	4480	Max. Ind.	3500	Max. Ind.	3300	Max. Ind.	2960	
Min. Ind.	4040	Min. Ind.	3280	Min. Ind.	3060	Min. Ind.	2660	

Lap Shear Strength
After 200 Hours
at 350 F

	325F	
	3270	CA
	3370	CA
	3240	CA
Avg.	3293.333	
Max. Ind.	3370	
Min. Ind.	3240	

Flatwise Tension

	RT		325F	
	650	CA	443.7	CA
	725	CA	425	CA
Avg.	687.5	Avg.	434.35	

"Facial" Scribed Panel	No Blisters	Slight Drip Marks
30 Day Salt Spray Exposure	No Peeling	No Creep From Scribe

Lap Shear Strength
After 30 Days
Salt Spray Exposure

	RT		
	3978	CA	No Bondline Corrosion
	4096	CA	No Bondline Corrosion
	4194	CA	No Bondline Corrosion
Avg.	4089.333		
Max. Ind.	4194		
Min. Ind.	3978		

Table A-11. CEDSABP Optimization Program, CEDSABP No. 8 (Cont.)

Lap Shear Bonds on Titanium		-67F		RT		325F		350F	
		3890	CP/APM	3580	CA/CP	3260	CA	3040	CA
		3600	CP/APM	3532	CA/CP	3490	CA	3040	CA
		3580	CP/APM	3330	CA/CP	3220	CA	2920	CA
	Avg.	3690	Avg.	3480.666	Avg.	3323.333	Avg.	3000	

Lap Shear Bonds on Titanium After 200 Hours at 350F		325F	
		3320	CA
		3540	CA
		3840	CA
	Avg.	3566.666	

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at	(1/e) value	Throwpower Poor to Fair.
10V	>40 sec	Coats heavy on Edges.
20V	>40 sec	Penetrates HC core 1/16".
30V	>40 sec	Lumpy coating.
40V	>40 sec	
50V	>40 sec	
60V	>40 sec	

Film Properties at	Thickness	Hardness
10v	-	9H
20V	0.15	9H
30V	0.3-0.7	9H
40V	0.2	9H
50V	0.4-0.7	9H
60V	0.4-1.1	9H

Lap Shear Strength After 200 Hours at 350 F On Aluminum		325F	
		3860	CA
		3840	CA
		3880	CA
	Avg.	3860	
	Max. Ind.	3880	
	Min. Ind.	3840	

Lap Shear Strength After 200 Hours at 350 F On Titanium		325F	
		3320	CA
		3180	CA
		3220	CA
	Avg.	3240	
	Max. Ind.	3320	
	Min. Ind.	3180	

APPENDIX A
Table A-12. CEDSABP Optimization Program, CEDSABP No. 9

Performance Parameter

Deposition Characteristics at	(1/e) value	Throwpower Excellent. Glossy coating.
10V	4.5 sec	Coats HC core completely.
20V	1.4 sec	
30V	0.8 sec	
40V	0.5 sec	
50V	0.3 sec	
60V	0.3 sec	

Film Properties at	Thickness	Hardness
10v	0.02	
20V	0.06	
30V	0.13	9H
40V	0.13	9H
50V	0.13	9H
60V	0.13	9H

Bell Peel Strength

	RT	
	14	CA
	14	CA
Avg.	14	

Lap Shear Strength

	-67F		RT		325F		350F	
	3620	CA/AP/CP	4026	CA/CP	3100	CA	2760	CA
	2920	CA/AP/CP	4020	CA/CP	3180	CA	2920	CA
	3500	CA/AP/CP	4189	CA/CP	3300	CA	2820	CA
Avg.	3346.6666	Avg.	4078.333	Avg.	3193.333	Avg.	2833.333	
Max. Ind.	3620	Max. Ind.	4189	Max. Ind.	3300	Max. Ind.	2920	
Min. Ind.	2920	Min. Ind.	4020	Min. Ind.	3100	Min. Ind.	2760	

Lap Shear Strength After 200 Hours at 350 F

	325F	
	3480	CA
	3340	CA
	3500	CA
Avg.	3440	
Max. Ind.	3500	
Min. Ind.	3340	

Flatwise Tension

	RT		325F
	712		422
	781		450
Avg.	746.5	Avg.	436

Scribed "Facial" Panels
30 Day Salt Spray

No blisters.   No drip marks.
No creep from scribe.
No peeling.

Lap Shear Strength After 30 Days Salt Spray Exposure

	RT		
	5306	CA	No bondline corrosion.
	5364	CA	No bondline corrosion.
	5226	CA	No bondline corrosion.
Avg.	5298.666		
Max. Ind.	5364		
Min. Ind.	5226		

Lap Shear Bonds		-67F		RT		325F		350F	
on Titanium		4600	CP/AP	4830	CP/AP	3040	CA	3120	CA
		4740	CP/AP	4754	CP/AP	3340	CA	2850	CA
		3920	CP/AP	4370	CP/AP	3600	CA	3040	CA
	Avg.	4420	Avg.	4651.333	Avg.	3326.666	Avg.	3003.333	

Lap Shear Bonds		325F	
on Titanium		3620	CA
After 200 Hours		3680	CA
at 350F		3600	CA
	Avg.	3633.333	

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at	(1/e) value
10V	4.5 sec
20V	2.0 sec
30V	1.1 sec
40V	0.7 sec
50V	0.7 sec
60V	0.7 sec

Throwpower Very good. Some decrease in throwpower.
Coating is slightly rough, darker than at 0 days.
Coats HC core comepletely at 40V.

Film Properties at	Thickness	Hardness
10v	-	-
20V	0.09 mils	9H
30V	0.16 mils	9H
40V	0.18 mils	9H
50V	0.185 mils	9H
60V	0.2 mils	9H

Lap Shear Strength		325F
After 200 Hours		3660
at 350 F		3640
On 2024-T81 Aluminum		3690
	Avg.	3663
	Max. Ind.	3690
	Min. Ind.	3640

Lap Shear Strength		325F
After 200 Hours		3030
at 350F		3220
on Titanium		3660
	Avg.	3297
	Max. Ind.	3660
	Min. Ind.	3030

Table A-13. CEDSABP Optimization Program, CEDSABP No. 10

Performance Parameter

Deposition Characteristics at (1/e) value		Throwpower Excellent. Glossy Coating.
10V	9.6 sec	Coats HC core completely.
20V	3.2 sec	
30V	1.4 sec	
40V	0.8 sec	
50V	0.5 sec	
60V	0.5 sec	

Film Properties at	Thickness	Hardness
10v	0.1	
20V	0.11	
30V	0.16	9H
40V	0.17	9H
50V	0.15	9H
60V	0.17	9H

Bell Peel Strength

	RT	
	14	CA
	14	CA
Avg.	14	

Lap Shear Strength

	-67F		RT		325F		350F	
	3600	CA/CP	3988	CA	3040	CA	2720	CA
	3620	CA/CP	3898	CA	3240	CA	3000	CA
	3600	CA/CP	3718	CA	3340	CA	3160	CA
Avg.	3606.6666	Avg.	3868	Avg.	3206.666	Avg.	2960	
Max. Ind.	3620	Max. Ind.	3988	Max. Ind.	3340	Max. Ind.	3160	
Min. Ind.	3600	Min. Ind.	3718	Min. Ind.	3040	Min. Ind.	2720	

Lap Shear Strength
After 200 Hours
at 350 F

	325F	
	3360	CA
	3200	CA
	3320	CA
Avg.	3293.333	
Max. Ind.	3360	
Min. Ind.	3200	

Flatwise Tension

	RT		325F	
	765	CA	438	CA
	698	CA	395	CA
Avg.	ERR	Avg.	416.5	

Scribed "Facial" Panels · Some slight pitting. · Slight drip marks
30 Day Salt Spray · No creep from scribe. · No Peeling.

Lap Shear Strength
After 30 Days
Salt Spray Exposure

		RT		
		4846	CA/CP	No bondline corrosion.
		4734	CA/CP	No bondline corrosion.
		4794	CA/CP	No bondline corrosion.
	Avg.	4791.333		
	Max. Ind.	4846		
	Min. Ind.	4734		

Lap Shear Bonds
on Titanium

	-67F			RT		325F		350F	
	3040	CP/AP		4754	CA/CP/AP	3180	CA	3200	CA
	3820	CP/AP		4338	CA/CP/AP	3120	CA	2980	CA
	3500	CP/AP		4234	CA/CP/AP	3160	CA	2800	CA
Avg.	3453.3333	Avg.		4442	Avg.	3153.333	Avg.	2993.333	

Lap Shear Bonds
on Titanium
After 200 Hours
at 350F

	325F	
	3600	CA
	3920	CA
	3700	CA
Avg.	3740	

Bath Stability Physical Properties After 30 Days, Stirring

Deposition Characteristics at (1/e) value		Throwpower:
10V	4.0 sec.	Excellent, completely coats core at 30V.
20V	3.6 sec.	Almost complete at 20V. Smooth, glossy
30V	2.0 sec.	film.
40V	1.2 sec.	
50V	0.9 sec.	
60V	0.7 sec.	

Film Properties at	Thickness	Hardness
10V	-	-
20V	0.07-0.12 mils	9H
30V	0.27 mils	9H
40V	0.33 mils	9H
50V	0.38 mils	9H
60V	0 27 mils	9H

Lap Shear Strength		325F
After 200 Hours		3700
at 350 F		3650
On 2024-T81 Aluminum		3820
	Avg.	3723
	Max. Ind.	3820
	Min. Ind.	3650

Lap Shear Strength		325F
After 200 Hours		3950
at 350F		3600
on Titanium		3800
	Avg.	3783
	Max. Ind.	3950
	Min. Ind.	3600

Table A-14. CEDSABP Optimization Program, CEDSABP No. 11

Performance Parameter

Deposition Characteristics at (1/e) value		Throwpower Excellent.
10V	2.2 sec	Thin uniform coating.
20V	1.5 sec	Completely coats HC core
30V	0.5 sec	at 30 V.
40V	0.8 sec	
50V	0.4 sec	
60V	0.5 sec	

Film Properties at	Thickness	Hardness
10V	-	-
20V	0.09 mils	9H
30V	0.11 mils	9H
40V	0.14 mils	9H
50V	0.13 mils	9H
60V	0.17 mils	9H

Bell Peel Strength	RT
	6
	6
	5
	6
Avg.	6

Lap Shear Strength		-67F		RT		325F		350F
		4100		3440		3220		2920
		4120		3740		3450		3150
		4200		3700		3420		3200
	Avg.	4140	Avg.	3627	Avg.	3363	Avg.	3090
	Max. Ind.	4200	Max. Ind.	3740	Max. Ind.	3450	Max. Ind.	3200
	Min. Ind.	4100	Min. Ind.	3440	Min. Ind.	3220	Min. Ind.	2920

Lap Shear Strength After 200 Hours at 350 F		325F
		3600
		3620
		3600
	Avg.	3607
	Max. Ind.	3620
	Min. Ind.	3600

Flatwise Tension		RT		325F
		803		452
		788		445
	Avg.	796	Avg.	448

Scribed "Facial" Panels 30 Day Salt Spray	No peeling No blistering No pits

Lap Shear Strength After 30 Days Salt Spray Exposure		RT
		4958
		4444
		4878
	Avg.	4760
	Max. Ind.	4958
	Min. Ind.	4444

Table A-14. CEDSABP Optimization Program, CEDSABP No. 11 (Cont.)

Lap Shear Bonds on Titanium	-67F	RT	325F	350F
	3600	4220	3650	3400
	3820	4300	3580	3250
	3650	3600	3400	3100
	Avg. 3690	Avg. 4040	Avg. 3543	Avg. 3250

Lap Shear Bonds on Titanium After 200 Hours at 350F	325F
	3700
	3440
	3550
Avg.	3563

Bath Stability Physical Properties After 30 Days Stirring

Deposition Characteristics at	(1/e) value
10V	4.75 sec.
20V	2.5 sec.
30V	2.7 sec.
40V	2.7 sec.
50V	2.0 sec.
60V	2.7 sec.

Throwpower: Excellent. HC core coated completely at 20-30V, smooth, uniform coating.

Film Properties at	Thickness	Hardness
10V	0.04 mils	9H
20V	0.08 mils	9H
30V	0.07 mils	9H
40V	0.10 mils	9H
50V	0.11 mils	9H
60V	0.12 mils	9H

Lap Shear Strength After 200 Hours at 350 F on 2024-T81 Aluminum	325F
	3760
	3760
	3720
Avg.	3747
Max. Ind.	3760
Min. Ind.	3720

Lap Shear Strength After 200 Hours at 350 F on Titanium	325F
	3720
	4000
	3890
Avg.	3870
Max. Ind.	4000
Min. Ind.	3720

GAS CHROMATOGRAPH ANALYSIS

B.1 Title: Gas Chromatographic Analysis of XA-3995

B.2 Scope: To Determine the Weight Percent of Solvents in this Primer

B.3 Equipment and Materials:

1 - #5840 Hewlett Packard GC, with or w/o Autosampler, or equivalent

1 - SS 1/8" D x 6' column with 10% CW 20M on 80/100 Suplecoport

1 - Four-place analytical balance

1 - 10.0 µl syringe

20 mL vials and polyseal caps

MIBK

Xylenes

Butyl celosolve

Toluene

THF

B.4 Step-by-Step Procedure:

(A) Equipment Settings

Install column from injection port "B" to FID port "B"

GAS CHROMATOGRAPH

Temp 1	MAX	200.0	40.0
Time 1		0.0	
Rate		20.0	
Temp 2	MAX	200.0	200.0
Time 2		10.00	
Inj. Temp	MAX	320.0	225.0
FID Temp	MAX	320.0	300.0
TCD Temp	MAX	320.0	300.0
CHT SPD		1.0	

GAS CHROMATOGRAPH ANALYSIS

Zero	10
Attn 2^	14
FID Signal	B
SLP SENS	5.00
Area Reject	400000
Flow A	20
Flow B	20

<u>Note</u>: Be sure to delete all previous ISTD and ESTD methods from instrument.

(B) <u>Solutions</u>

    (1) Standard for <u>I</u>nternal <u>ST</u>andar<u>D</u> Method

        a. Weight in a polyseal capped vial:

MIBk	0.2 grams
Xylenes	0.2 grams
Butyl cellosolve	0.2 grams
Toluene	0.2 grams
THF	20.0 grams

    (2) Unknown Sample Preparation

        a. Weight to four places in a polyseal capped vial:

XA-3995	10.0 grams
THF	10.0 grams
Toluene	0.1 grams

GAS CHROMATOGRAPH ANALYSIS

(C) Calibration-Internal Standard Method

(1) The ISTD standard is run at least twice to calibrate the instrument.

(2) With the program installed, inject 2μl of ISTD standard and start the run. When the run is complete and printout is obtained, punch **CALIB ISTD**. The instrument will then request **% RTW:** Enter 5. Then the instrument will ask for the retention time of the first peak of interest. (This is always the ISTD peak at about 3.5 minutes.) Enter the time and then the actual weight of Toluene in the standard sample. The next instrument query will be for the retention time and the amount for the second peak of interest, the MIBK peak. Enter time and amount for the MIBK peak. (The MIBK peak will be at about 3.1 minutes.) Next enter R.T. for Xylenes (about 4.3) and the amount. Finally, enter the R.T. for Butyl cellosolve (6.3) and the amount. For the next retention time query, punch **ENTER** and the machine will ask for a dilution factor. Enter 1.0 for the dilution factor. Finally, the instrument will ask for an **ISTD AMT**. Enter the weight of the Toluene in the sample and lastly, the sample amount. Enter 0 for the sample amount. This terminates the calibration dialogue and the first calibration run is complete. Punch ISTD to verify the data that has been entered. To average successive calibration runs, enter **CALIB n ENTER** after each additional run. In this case, n equals the number of calibration runs minus 1. After the second calibration run, type in **CALIB 1 ENTER** and after the third calibration run, enter **CALIB 2 ENTER** and on.

GAS CHROMATOGRAPH ANALYSIS

(D) <u>Sampling Testing</u>

    (1) Internal Standard Method

        a.   Punch ISTD AMT, enter weight of Toluene (ISTD) added to the sample and the weight of the sample without ISTD added (sample amount).

        b.   Inject 2 µl of sample and start run.

        c.   The instrument will report weight percent of each of the solvents directly at the end of each run.

B.5   <u>Data Reporting:</u>

$$\text{Wt. \% sol. in sample} = \frac{\text{A. sol x amount/A sol.}}{\text{A. ISTD x amount/A ISTD}} \times \frac{\text{amount of ISTD}}{\text{Sample amount}} \times 100$$

$$A = \text{Area} \qquad \text{sol.} = \text{solvent} \qquad \text{Wt.} = \text{weight}$$

APPENDIX C

LITERATURE SURVEY

The data gathered from the technical literature search was minimal. For the last 10-year period, the literature is sparse for 350°F cure water-base spray applied primer materials. References found on water-base polymeric materials are listed below:

- US 4049596, Corrosion-resistant aqueous and solvent-based primer -- pigments. CA 89 (4) 26132g

- US 4197219, Aqueous polyurethane-phenolic-formaldehyde resin -- surface coatings. CA 93 (6) 48164d

- US 4108811, Composition process for aqueous base coatings for corrodible metals. CA 90 (10) 73385X

- US 4564648A, Epoxy graft crylic water-base primer surfaces. CA 104 (18) 150927n

- DE 2903311, Stable aqueous composition for coating metal surfaces. CA 92 (16) 125016V

- JP 8313665 A2, JP 5813665, Aqueous primers for metals. CA 99 (10) 7230 ЗW

- JP 84199776A2, Water-base primers. CA 102 (20) 168370u

- Journal: Proc.-Int. Conf. Org. Coat. Sci. Technol,; 4th, Date 1978, Pages 149-186, "The influence of water-soluble polymers on the application performance of water-borne coatings." CA 90 (8) 56362Y

- Journal: Zinc Phosphate and Strontium Chromate in Water-Base Anticorrosion Primers. CA 90 (8) 56380z

- Report: Water-base coatings. CA 87 (18) 137385v

APPENDIX D

FAILURE ANALYSIS - TASK III BONDED SPECIMENS

In Specimen #1, 2024-T81 adherends bonded with RB-398 adhesive. This
specimen is from a group which had an average failing stress of 1290 psi
at 350°F (Table 4-19). Photograph #1 shows where EDAX scans "A," "B,"
and "C" were taken. Location "A" was found to contain very high
concentrations of aluminum with lesser amounts of silicon, oxygen and
carbon. The topography shown suggests possible aluminum oxide which may
have been pulled from the opposite surface or, more likely, aluminum
particles which are used in the adhesive formation plus organic material
with silicon as used in the adhesive formulation.

Location "B" is markedly low in aluminum content but contains noticeably
high amounts of carbon, oxygen and zinc. This suggests principally
primer composition. Location "C" is high in aluminum and contains lesser
amounts of carbon, oxygen and zinc. This suggests a thin layer of primer
composition atop the aluminum adherend surface. It appears that fracture
occurred through the primer layer which agrees with observations made of
the same specimen using optical microscopy.

Photograph #2 is an X-ray element map of the element zinc on the surface
of the primer outside of the bond-line. The zinc concentration is shown
to be fairly abundant and dispersed.

In Specimen #2, 2024-T81 adherends bonded with AF-131 adhesive. This
specimen is from a group which had an average failing stress of 2660 psi
at 350°F (Table 4-17). Photograph #3 shows where EDAX scans "D" and "E"
were taken. Location "D" is high in aluminum with small amounts of
carbon and oxygen. Zinc is not present. This suggests a failure at the
metal surface/aluminum oxide layer as evidenced by the presence of
copper. The aluminum oxide layer location "E" is high in carbon,
silicon, and sulfur with a lesser amount of oxygen and a trace of
magnesium present. This composition suggests adhesive matrix material.
The topography of "E" and the absence of zinc and aluminum suggest
cohesive fracture areas whereas the adjacent surfaces, Location "D,"
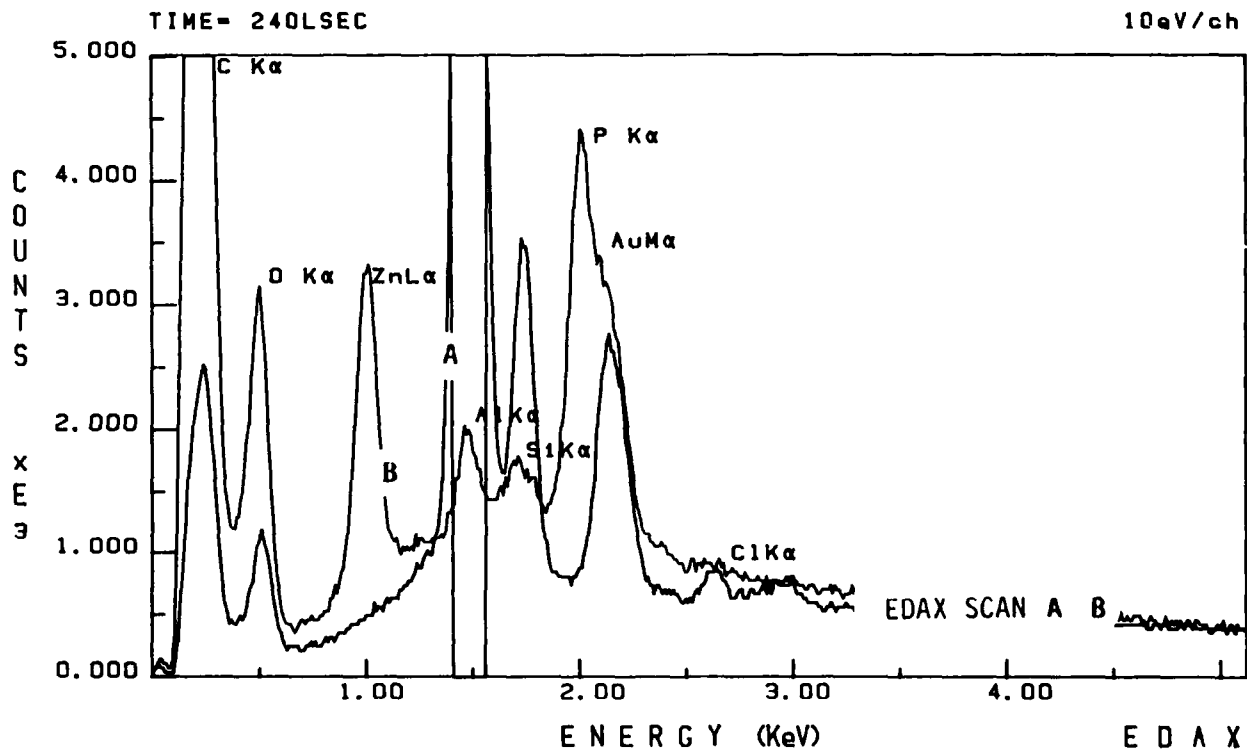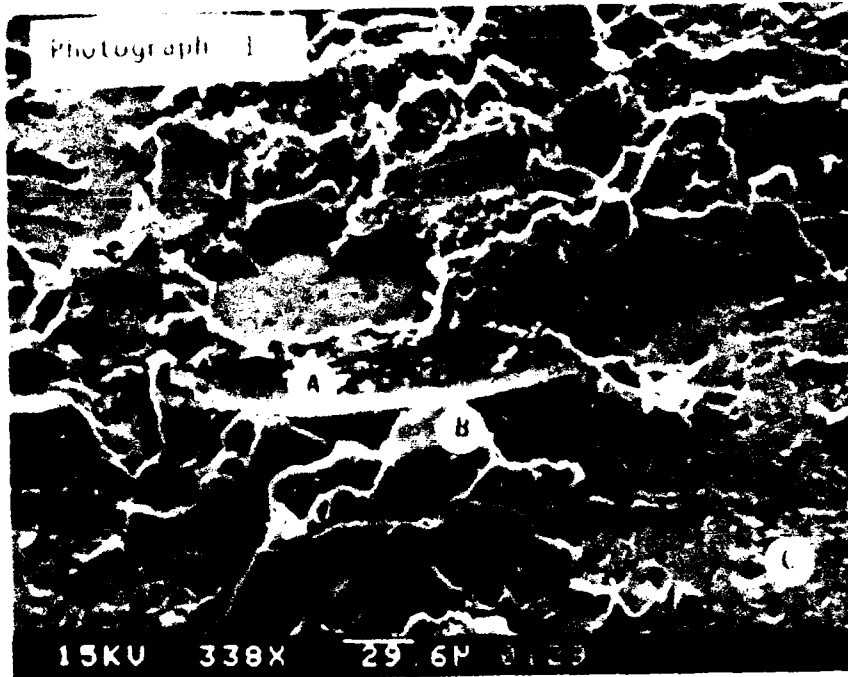
FAILURE ANALYSIS - TASK III BONDED SPECIMENS
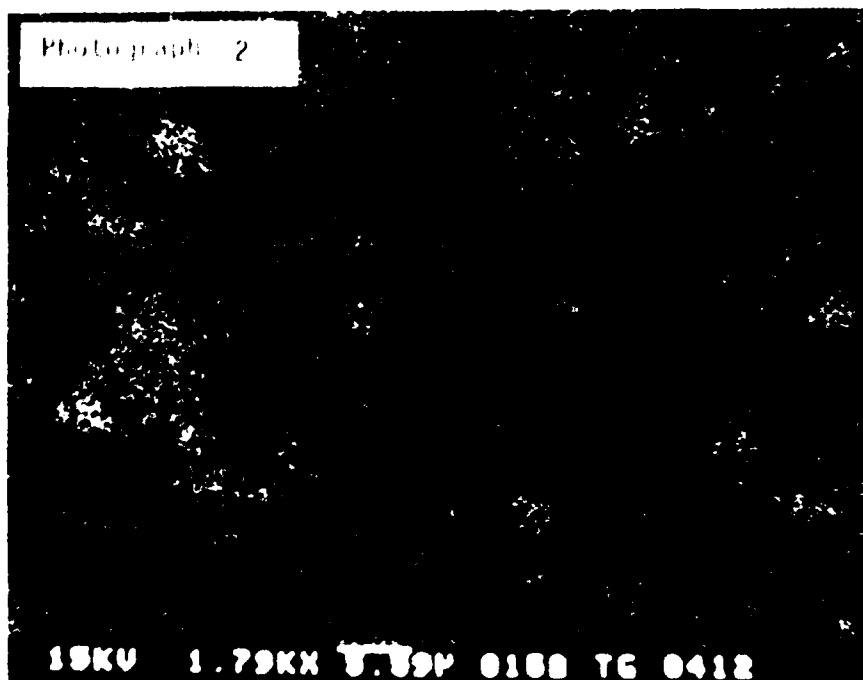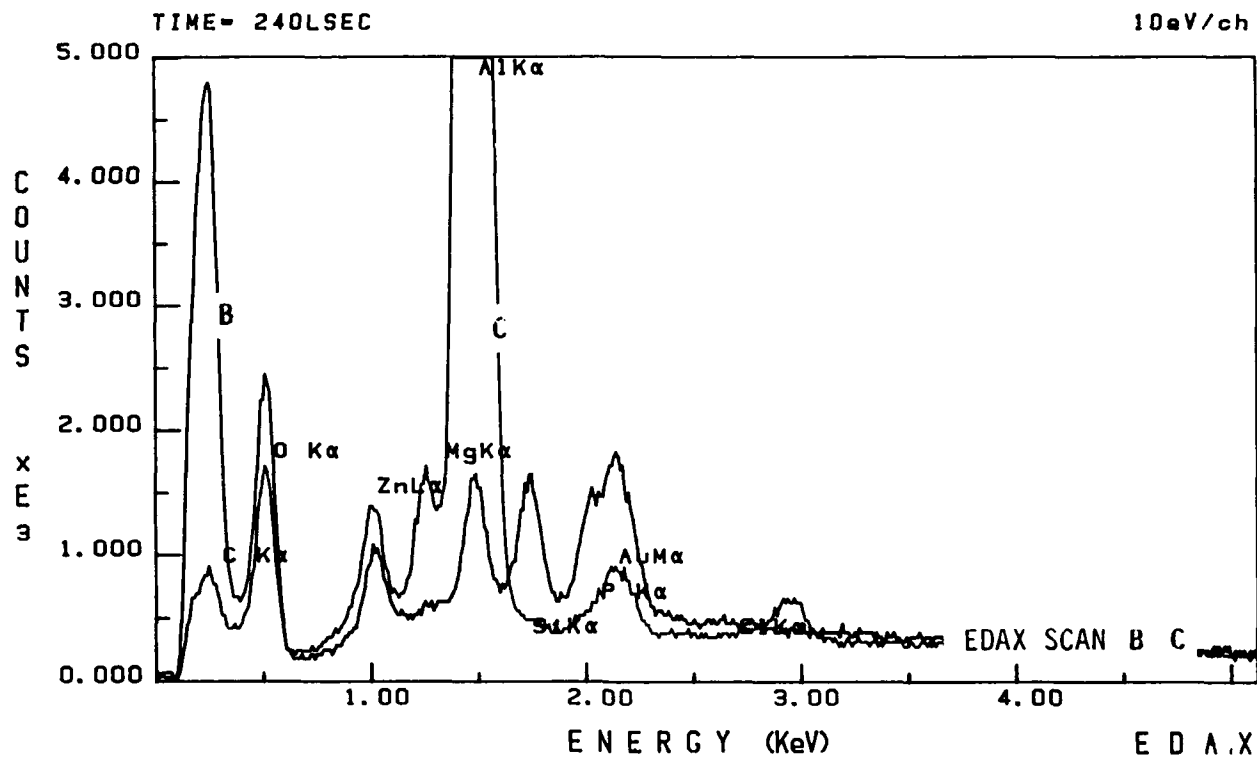
FAILURE ANALYSIS - TASK III BONDED SPECIMENS

FAILURE ANALYSIS - TASK III BONDED SPECIMENS
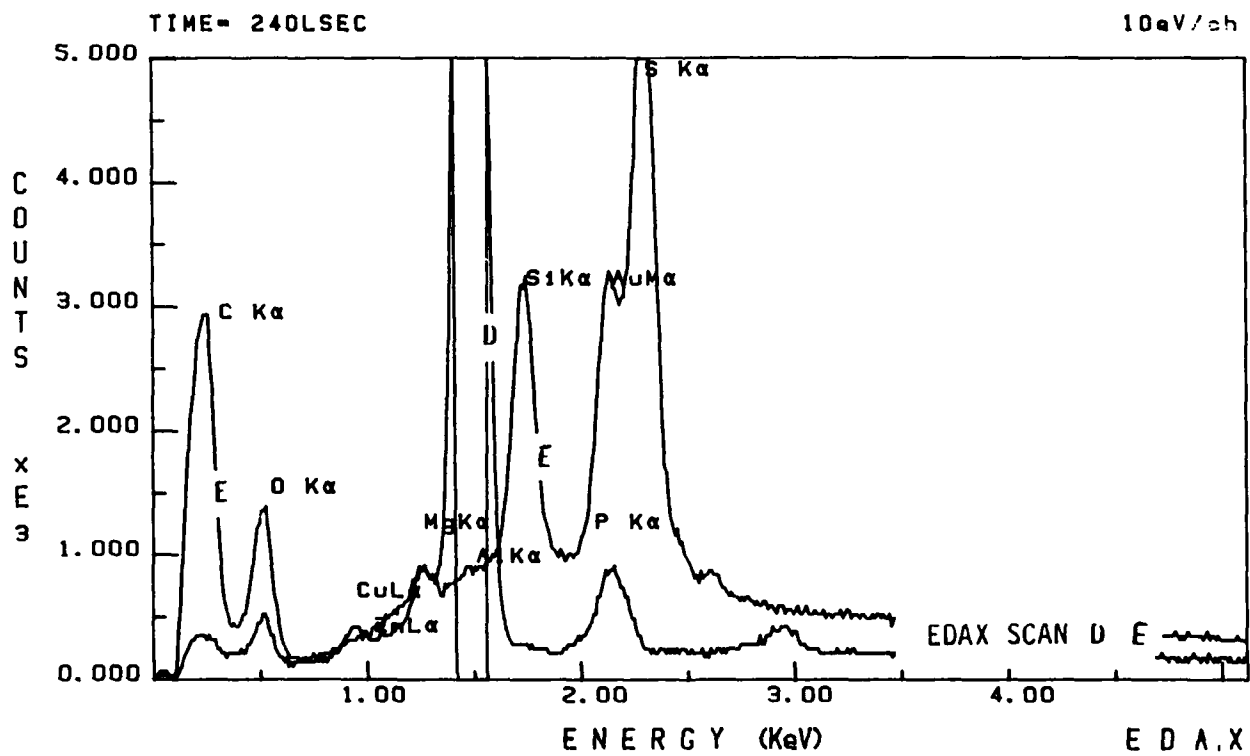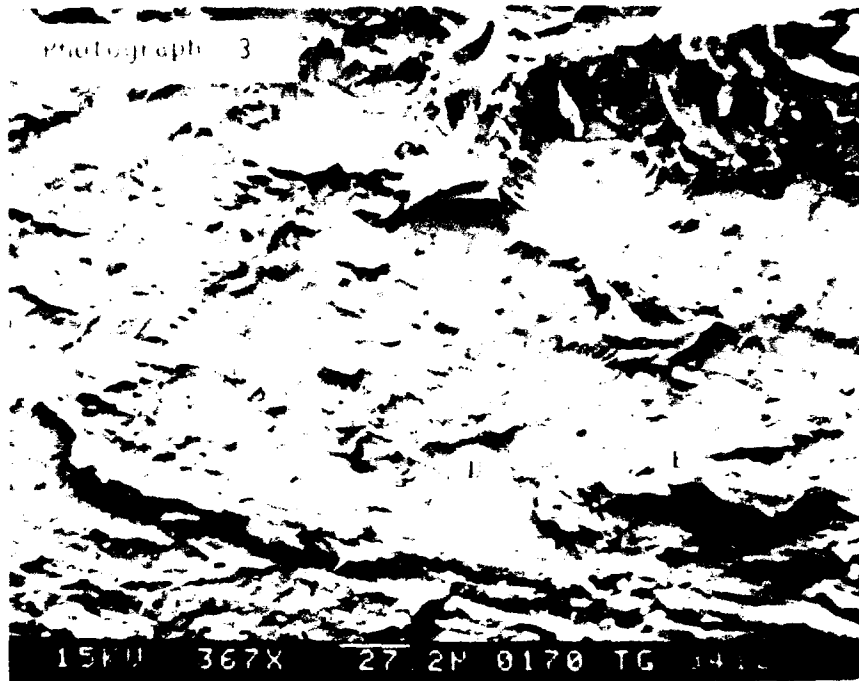
FAILURE ANALYSIS - TASK III BONDED SPECIMENS

suggest failure at/in the metal oxide interface. Zinc, as found in the preceding specimens, was not readily seen. Photograph #4 shows the primer surface outside of the bond-line with a heavy concentration of particulate matter.

Photograph #5 is an X-ray map of the element zinc which corresponds well with the particulate matter observed.

Photograph #6 is an X-ray map of the element aluminum for the same area examined for zinc. It appears in the photograph that the primer layer is extremely thin in these areas as evidenced by penetration to the aluminum surface, and that the zinc component of the primer has agglomerated somewhat.

In Specimen #3, 7075-T6 adherend bonded with AF-131 adhesive. This specimen is from a group which had an average failing stress of 3050 psi at -67°F (Table 4-19). Photograph #7 shows where EDAX scans "M" and "N" were taken. Scan "M" is of the adhesives flash exterior of the bond-line and scan "N" is the primer area exterior of the bond-line. Photograph #8 is the X-ray element map for zinc for the same area as Photograph #7. Photograph #9 is the X-ray map for aluminum for the same area. The noise level for aluminum is approximately the same as for zinc in the adhesive area and as such, neither element is judged to be present (see EDAX scan "M" and "N"). EDAX Scan "N" shows some aluminum which is corroborated by the X-ray map indicating a thin primer layer. The primer pigment component appears well distributed, but no comparison with other specimens regarding particulate size is possible due to the lower magnification used. Photograph #10 shows the failure surfaces of Specimen No. 3. The EDAX scans of Area "O" of Photograph #10 shows high aluminum content and some zinc plus carbon and oxygen. Zinc is a component of 7075-T6 alloy; however, we believe that the zinc present is contributed principally by the primer as shown by the amount of carbon and another element
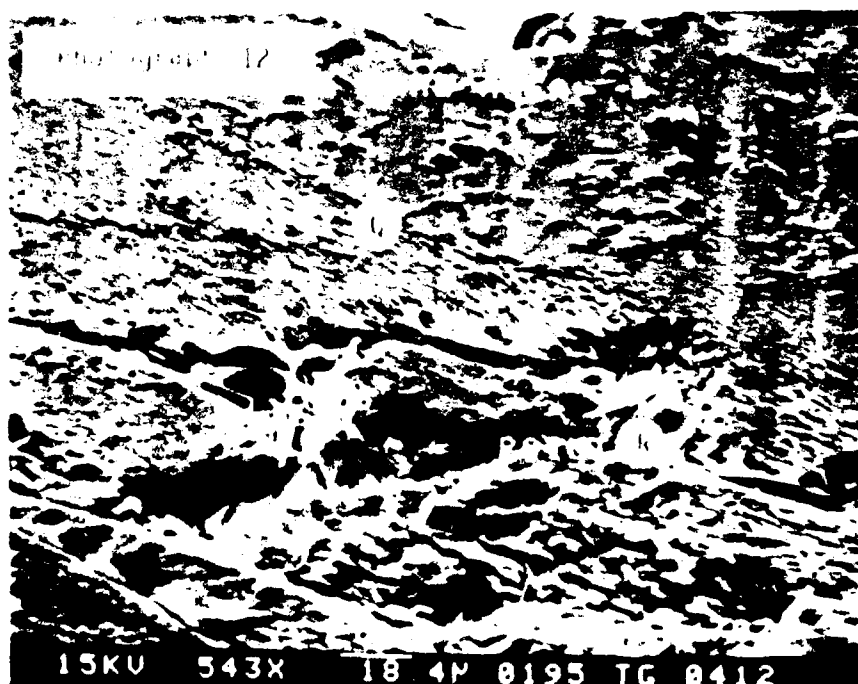
FAILURE ANALYSIS - TASK III BONDED SPECIMENS

Photograph 4
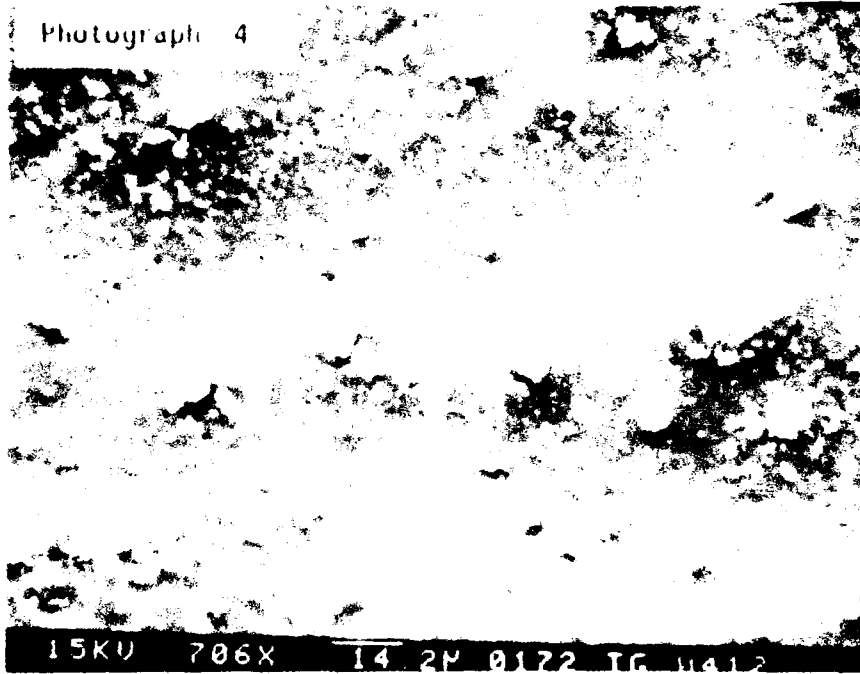
Photograph 5
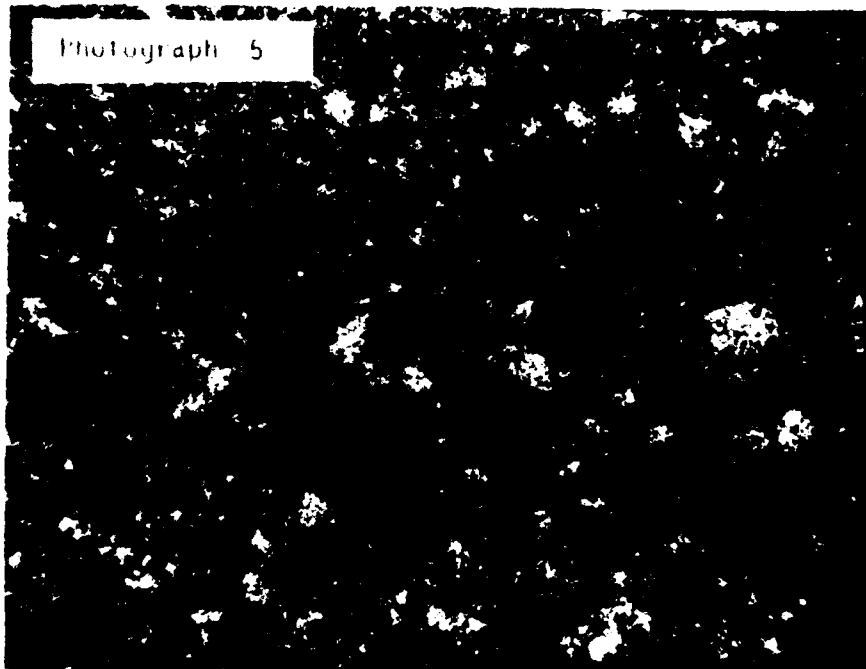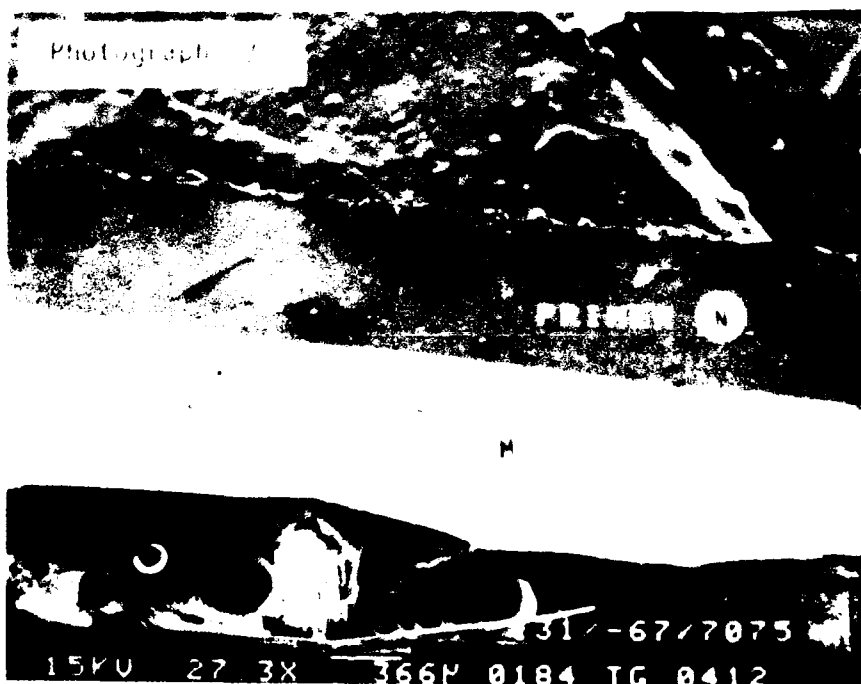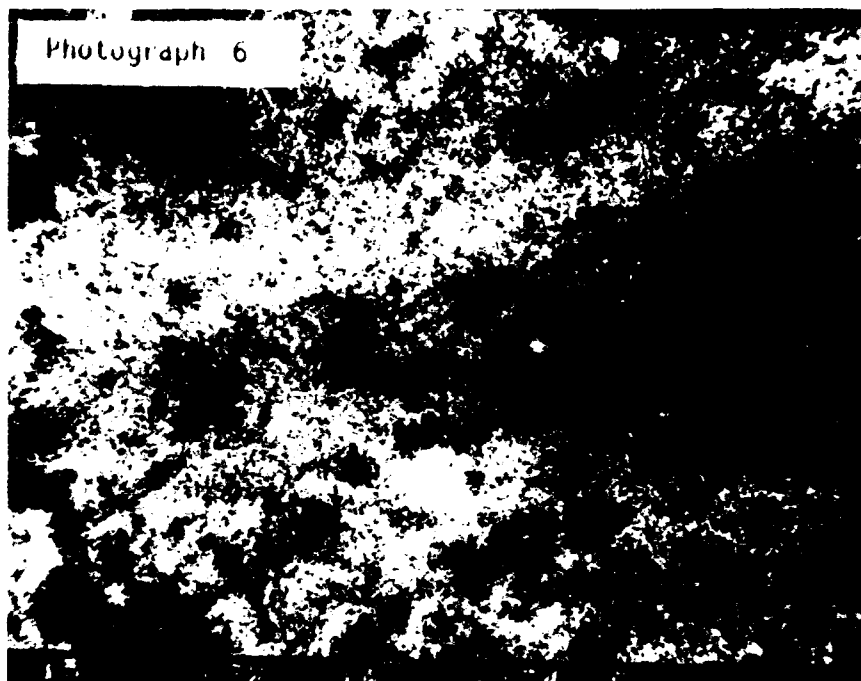
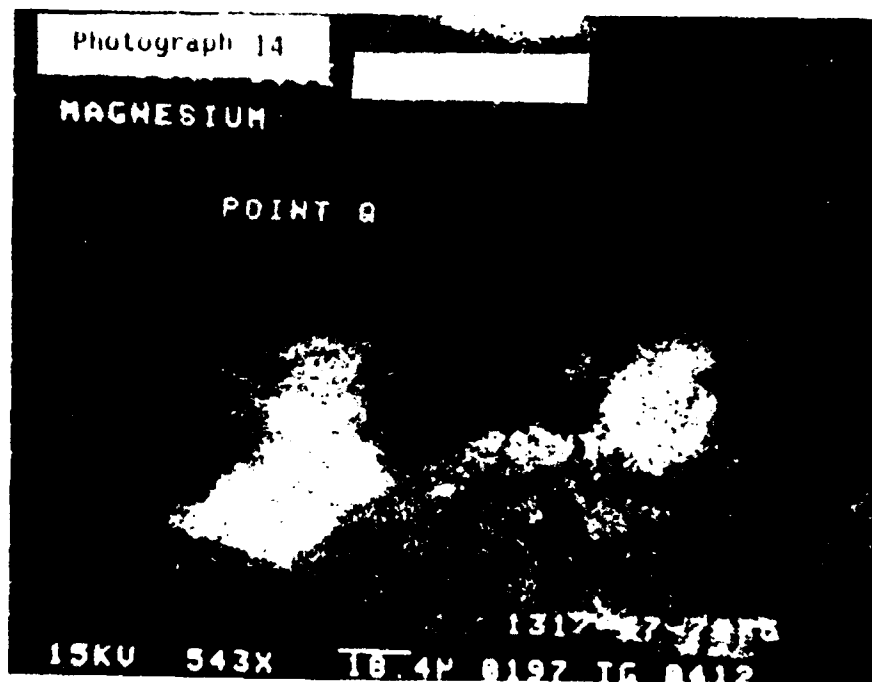FAILURE ANALYSIS - TASK III BONDED SPECIMENS

Photograph 6

Photograph 7

FAILURE ANALYSIS - TASK III BONDED SPECIMENS

Photograph 8

Photograph 9
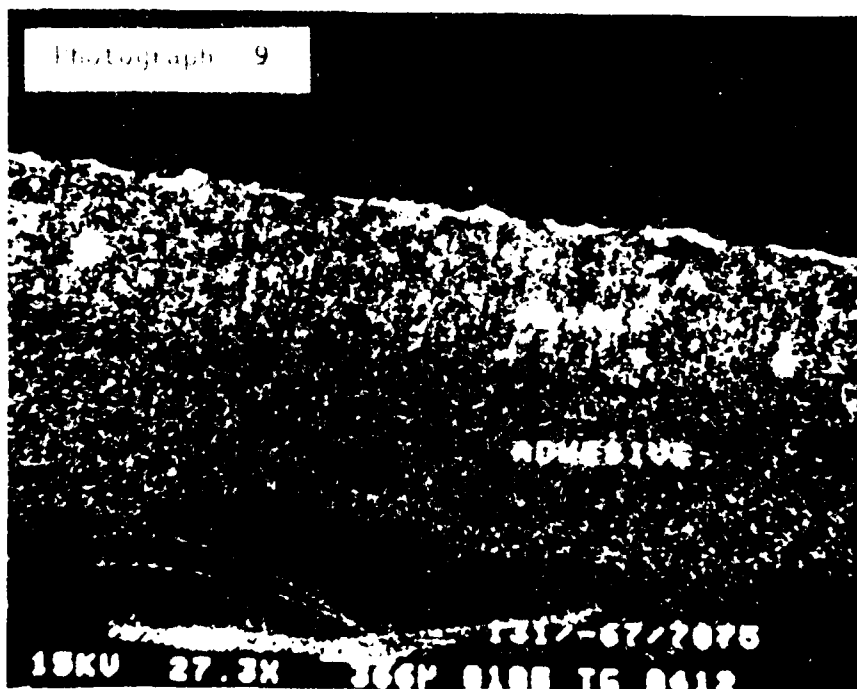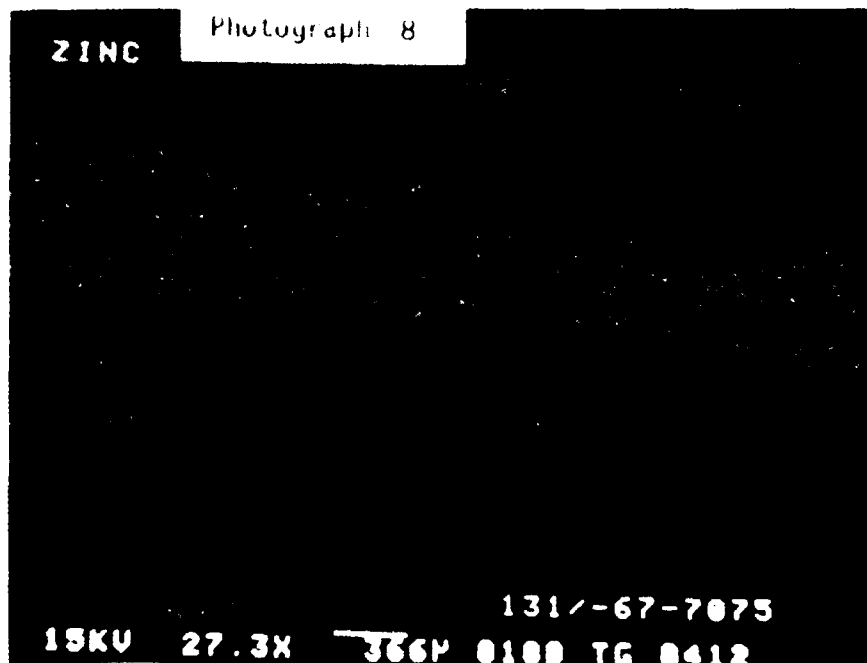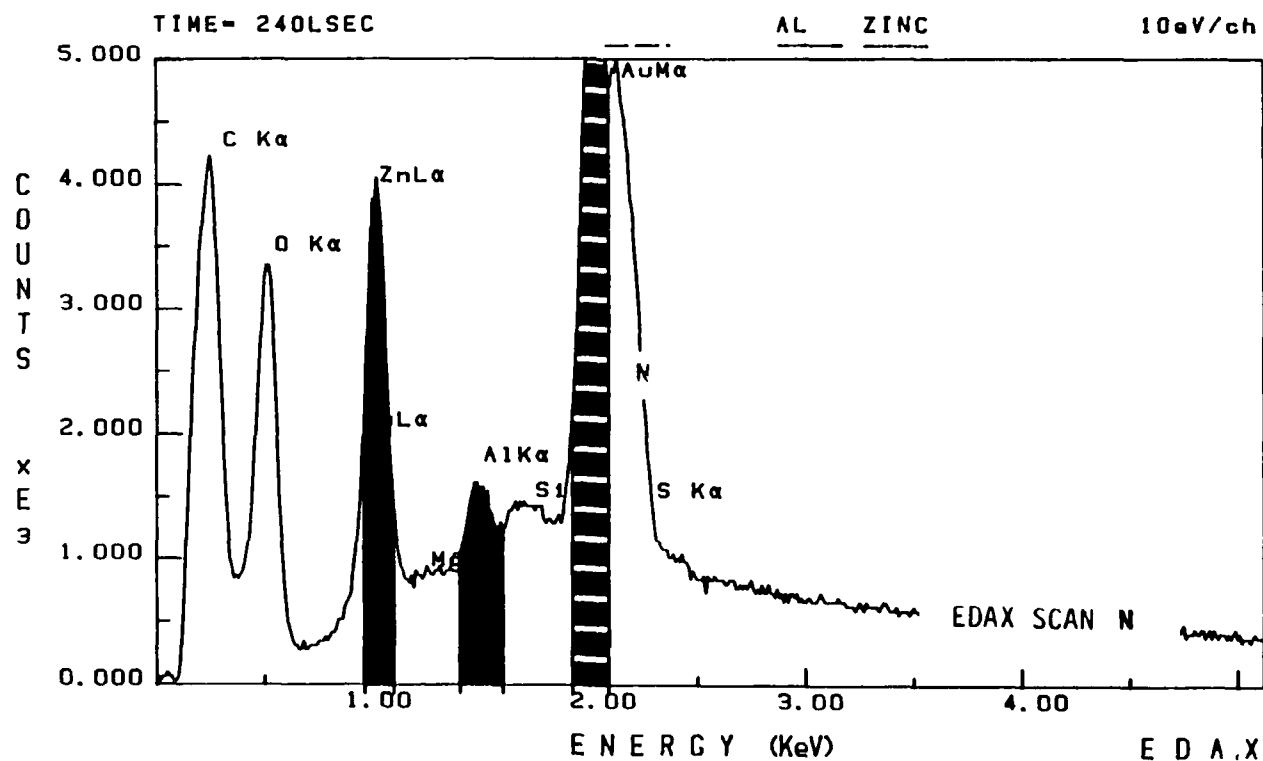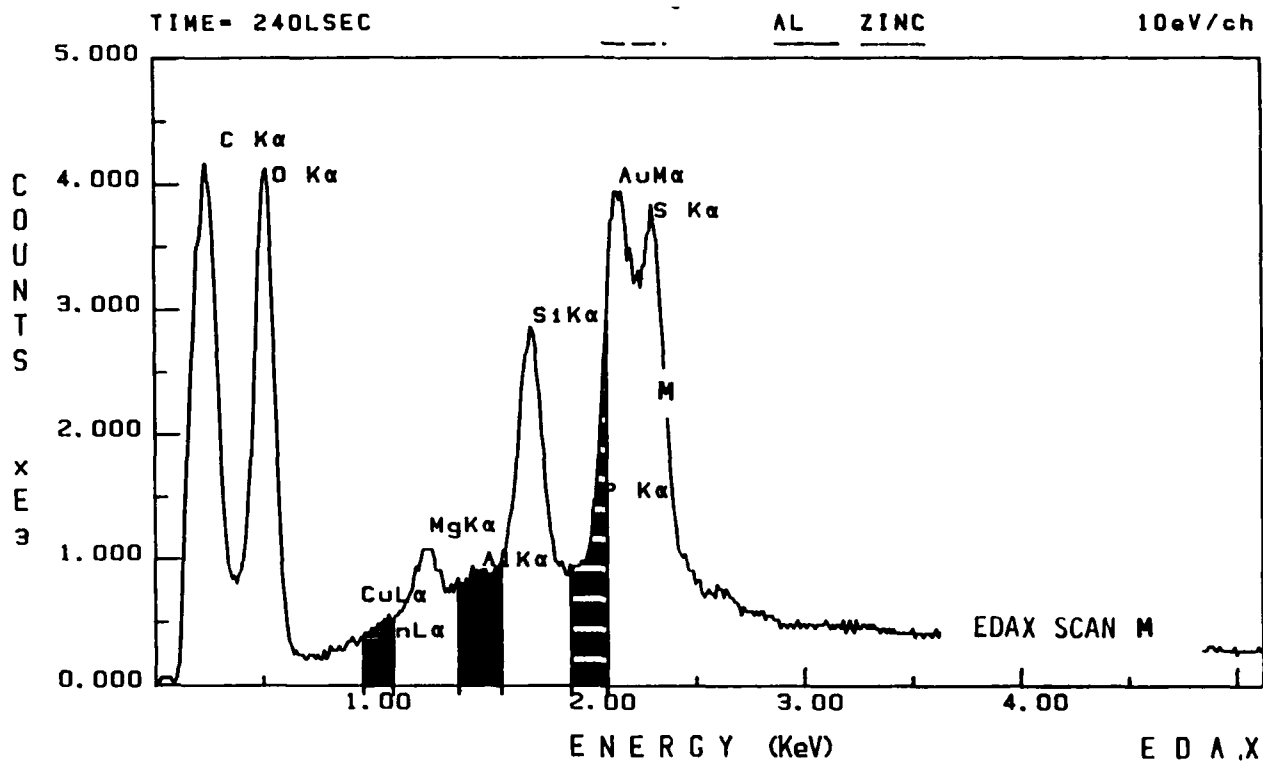
FAILURE ANALYSIS - TASK III BONDED SPECIMENS

FAILURE ANALYSIS - TASK III BONDED SPECIMENS
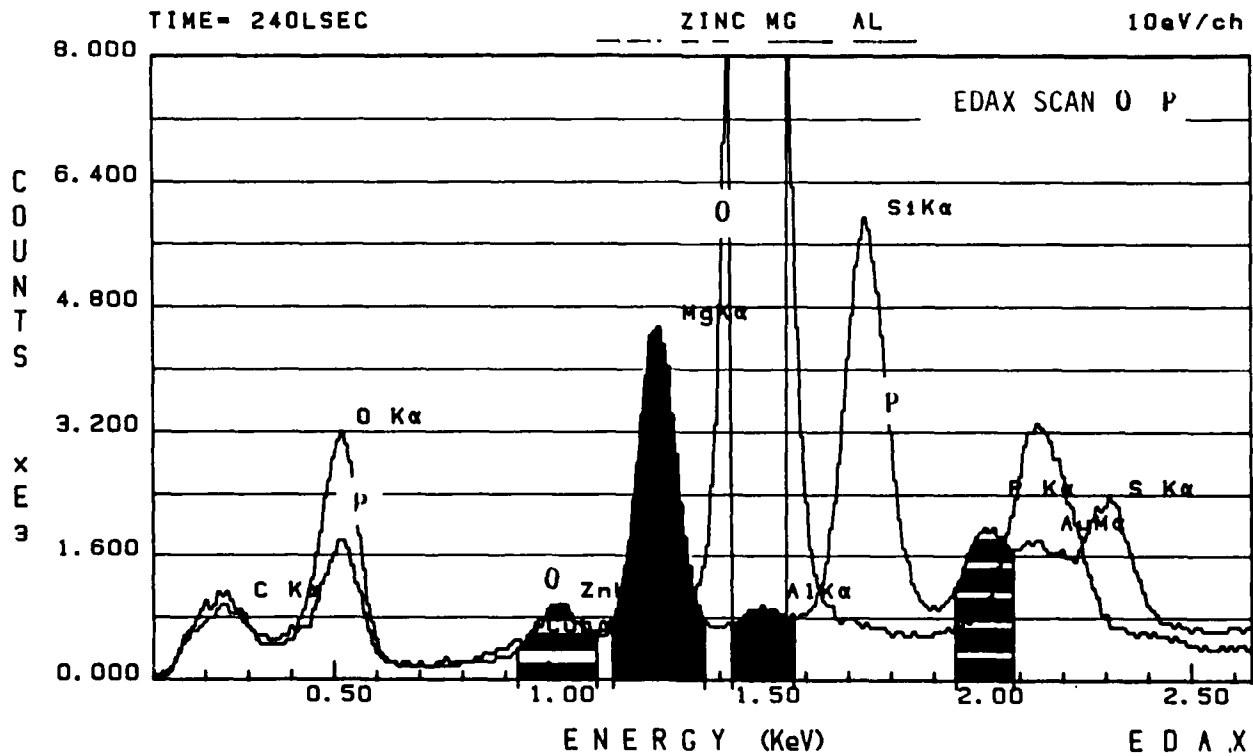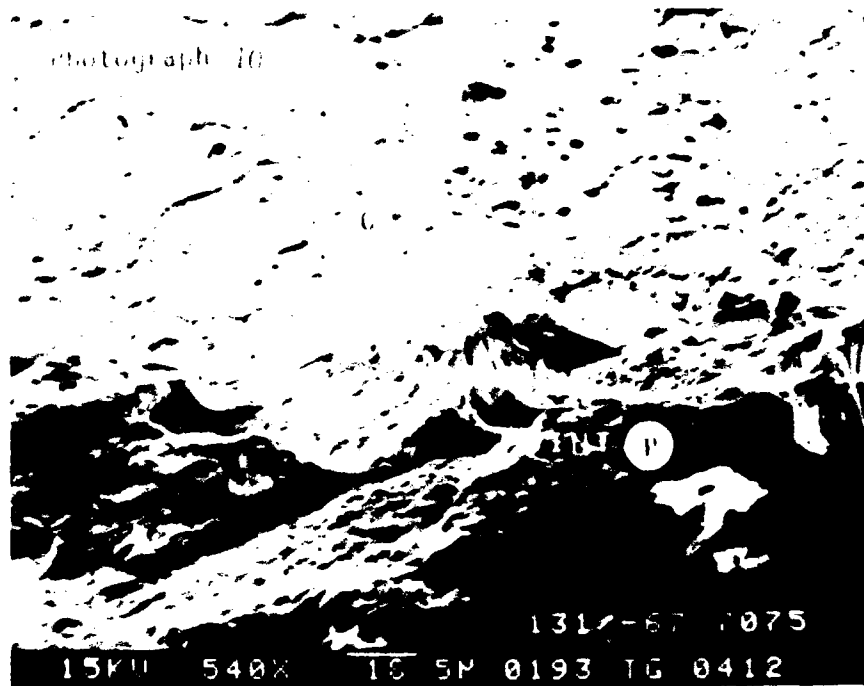
FAILURE ANALYSIS - TASK III BONDED SPECIMENS

which are present. The failure appears to be at/through the aluminum oxide/primer interfaces.

EDAX scan "P" shows carbon, oxygen, and high silicon and magnesium. Area "P" is adhesive resin; silicon is probably contributed by silicon dioxide, a common filler material used in adhesive formulations. The presence of high magnesium is unexplained. An X-ray map (Photograph #11) of the element aluminum for Photograph #10 corroborates the topography and EDAX scans "O" and "P."

The failure mode in the adhesive area appears to be cohesive, since no surface evidence of aluminum or zinc is present. Photograph #12 shows the fracture surface from the side opposite from Photograph #10. The EDAX scan of area "Q" shows high carbon and oxygen with some zinc and aluminum which further indicates the failure occurring at/through the aluminum oxide/primer interface. Photograph #13 shows the X-ray map for zinc for Photograph #12 and a relatively even distribution of zinc. Also seen in Photograph #12 at area "R" is what appears to be a fibrous topography. EDAX scan "R" shows high silicon and magnesium; Photograph #14 is the X-ray map for magnesium and shows a heavy concentration of this element in the areas showing fibrous topography.

In Specimen #4, 6-4 Titanium "T" peel specimen bonded with RB-398. These particular specimens failed during preparation (cutting to dimension). Photograph #15 shows the topography at the predominantly adherend surface. EDAX scan Al of this surface shows very high titanium with some aluminum, the principal alloying elements of the adherend. No zinc is present in this scan. Scan A2 is of the opposing surface (Photograph #16) of the adhesive topography and shows the normal carbon, oxygen, silicon and aluminum (filler particles) composition of RB-398 adhesive. Also present is zinc, which indicates that some primer material is present. An extended scale of EDAX scan area A2 shows titanium, which indicates that some of the titanium oxide layer has

FAILURE ANALYSIS - TASK III BONDED SPECIMENS

Photograph 11
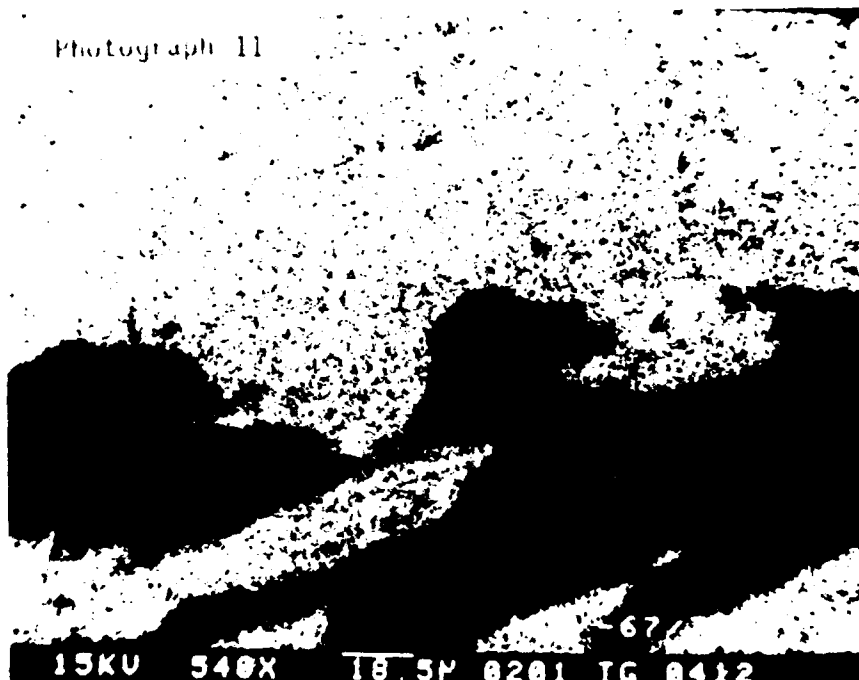
FAILURE ANALYSIS - TASK III BONDED SPECIMENS

Photograph 13

FAILURE ANALYSIS - TASK III BONDED SPECIMENS

Photograph 14

MAGNESIUM

POINT Q

15KV   543X

Photograph 15

A₁

15KV   100X   100P 0246 TG
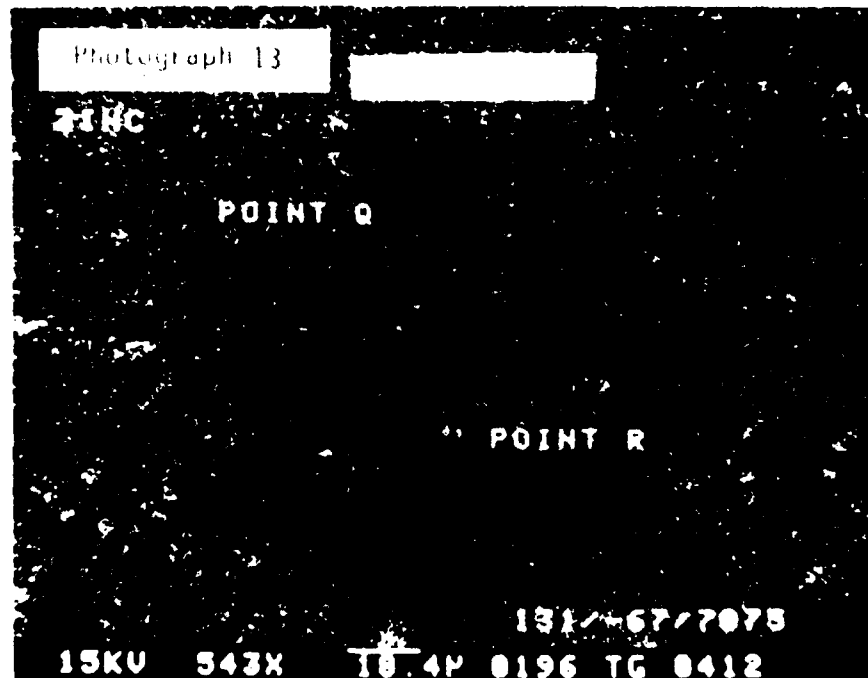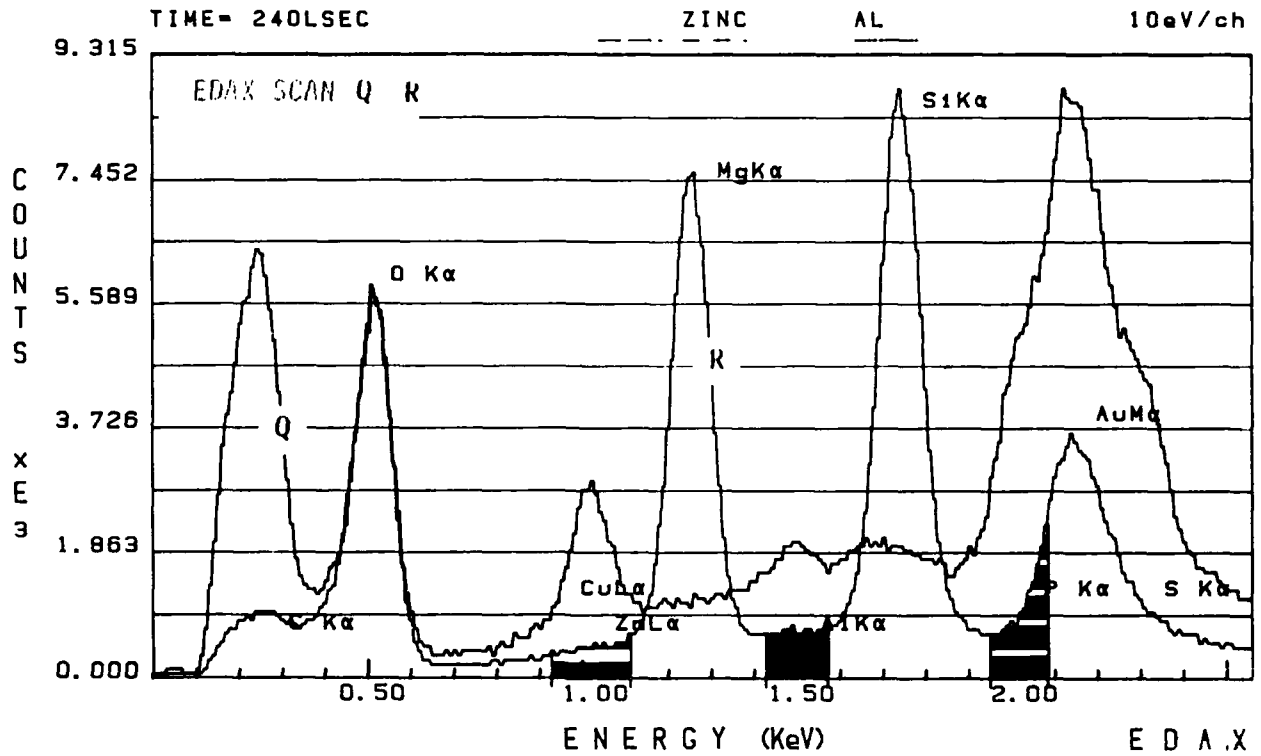
FAILURE ANALYSIS - TASK III BONDED SPECIMENS

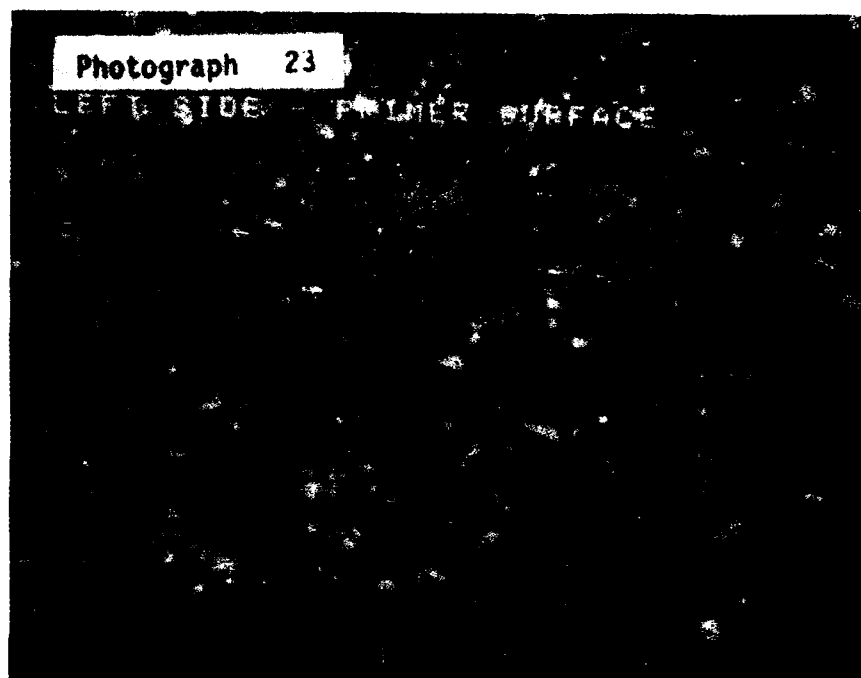Photograph 16
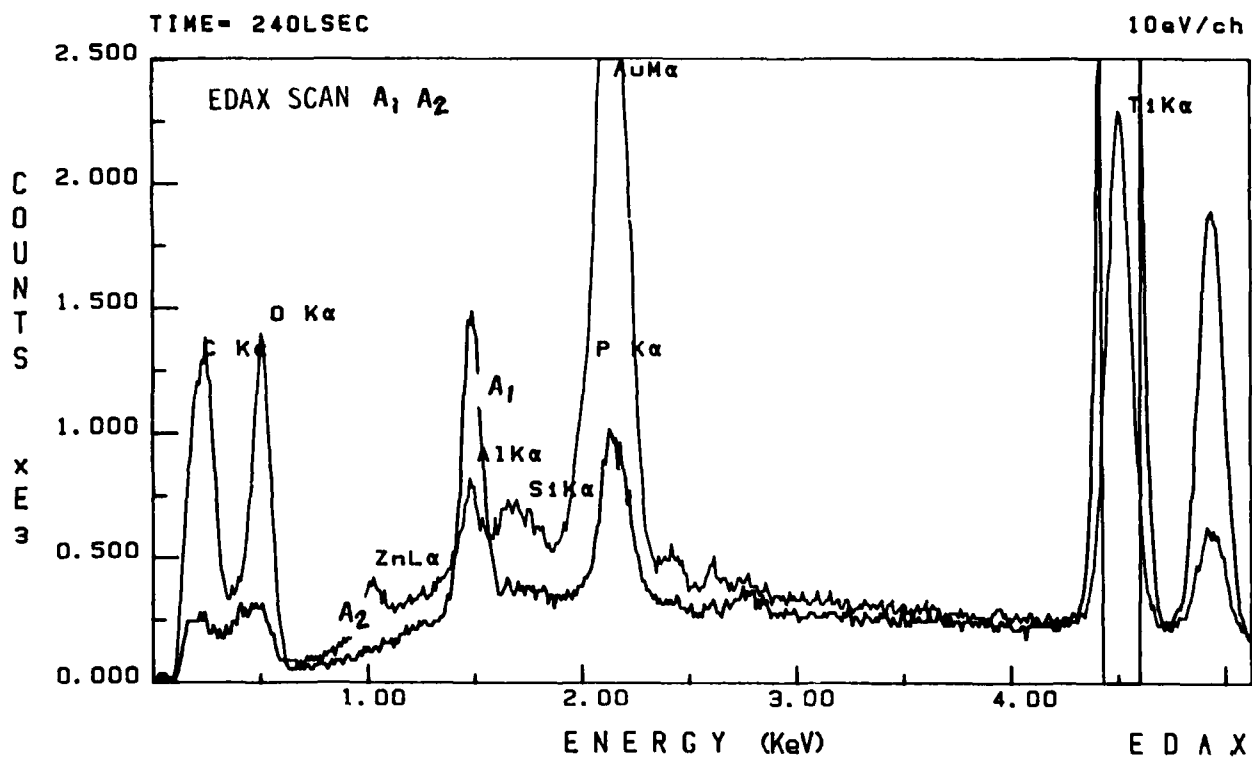
FAILURE ANALYSIS - TASK III BONDED SPECIMENS

separated with the adhesives. The failure, therefore, appears to be more
in the oxide layer of the titanium adherend than in the primer layer.

In Photograph #17, the topography of the primer coat outside the bond-
line is shown. Particle distribution is fairly uniform and quite dense.
Photograph #18 is the X-ray map for the element zinc which corresponds to
the area shown in Photograph #17. The primer coating on this specimen
appeared to be thicker than some of the other specimens examined. X-ray
mapping for titanium did not reveal any thin areas in the primer.

In Specimen #5, 2024 aluminum bonded with AF-131 by 3M. This specimen is
reported to have failed at 2866 psi. Photographs #19 and #20 show areas
of matching topography (right- and left-hand surfaces of lap shear
specimen) which appear to have a large amount of cohesive failure but
also show a predominantly adhesive layer side (right) and a predominantly
substrate side (left). The EDAX scans for Area "A_3" (substrate side) and
area "B_3" (adhesive side) appear quite similar. The adhesive surface
shows more zinc and much less aluminum present than the substrate
surface. Photograph #21 is a closer view of the adhesive surfaces and
Photograph #22 is an X-ray map of Photograph #21 surface for the element
aluminum. Numerous aluminum concentrations are seen which we think are
due to aluminum oxide. The failure mode of sample #5 appears to be
principally cohesive with some interfacial failures occurring in/at the
oxide/adherend interface. Photograph #23 shows the topography of the
primer outside the bond-line. Particulate matter is quite uniform and
dense. Photograph #24 is an X-ray map for the element zinc which
corresponds to the area shown in Photograph #23. X-ray mapping for
aluminum did not reveal any thin areas.

TIME= 240LSEC
10eV/ch

EDAX SCAN A₂

Photograph 17

Photograph 18

ZINC ELEMENT MAP

15KV 787X 12.7µ 0299 TG

Photograph 19

Photograph 20

TIME- 240LSEC   10eV/ch

EDAX SCAN A₃ B₃

ENERGY (KeV)   E D A .X

Photograph 21

Photograph 22

RIGHT SIDE PRIMER + ADHESIVE

Photograph 23
LEFT SIDE - PRIMER SURFACE

Photograph 24
LEFT SIDE
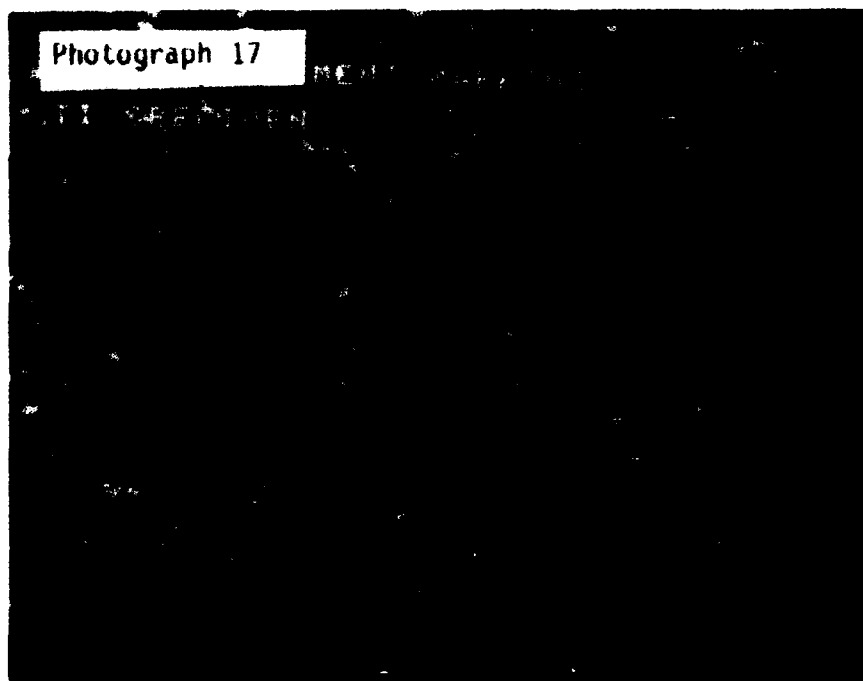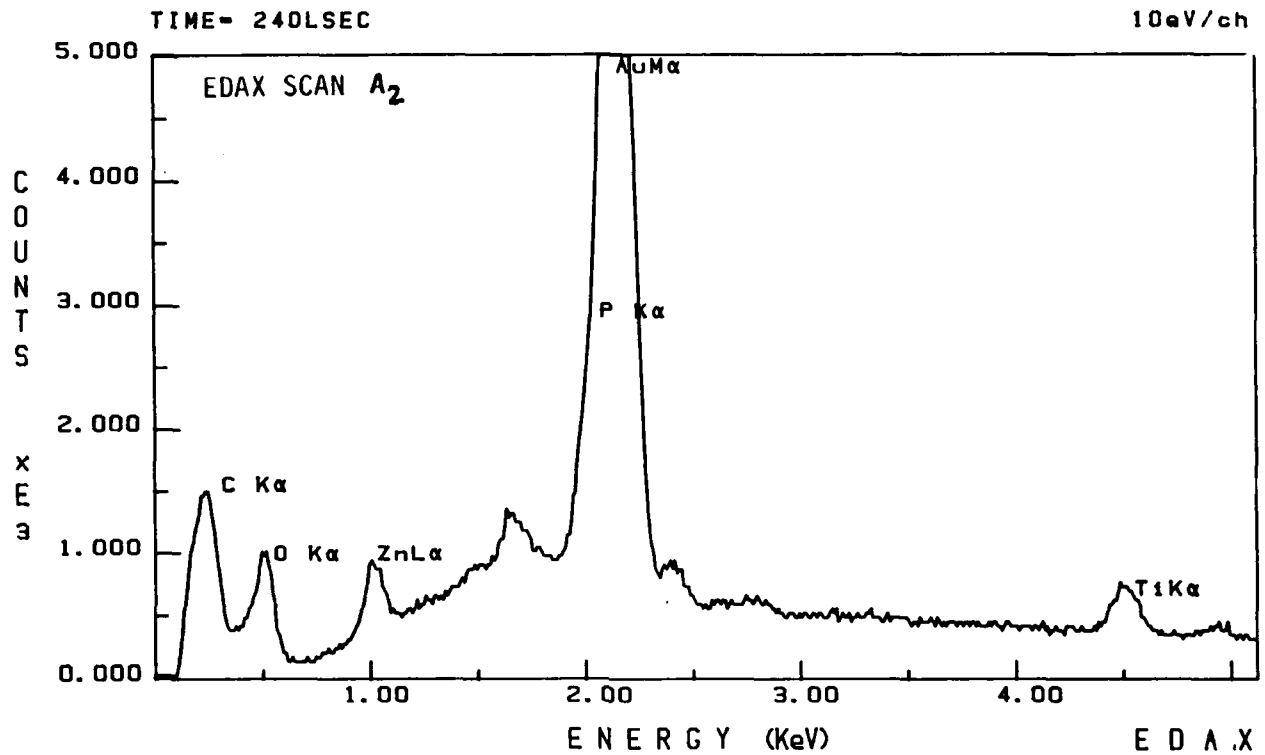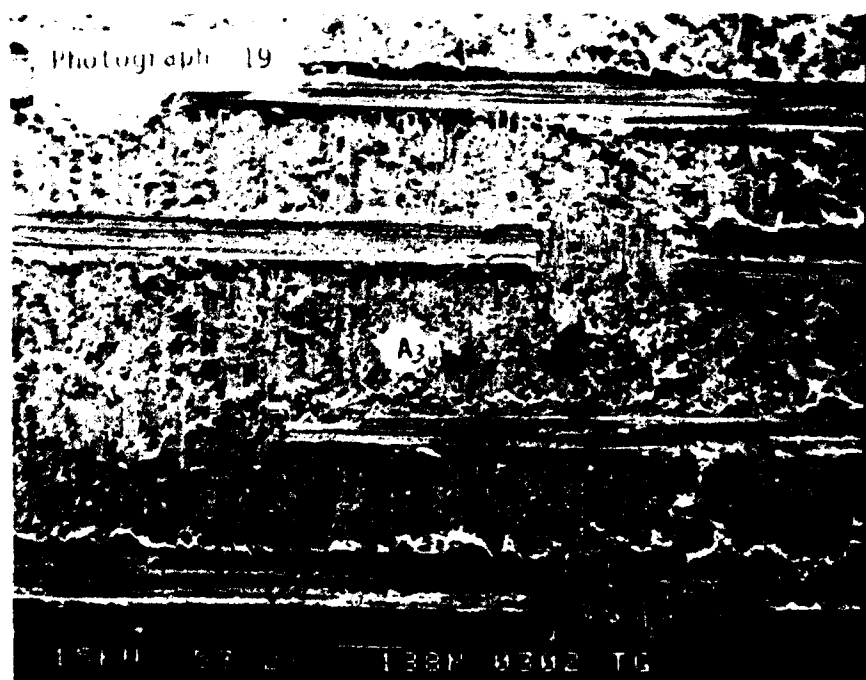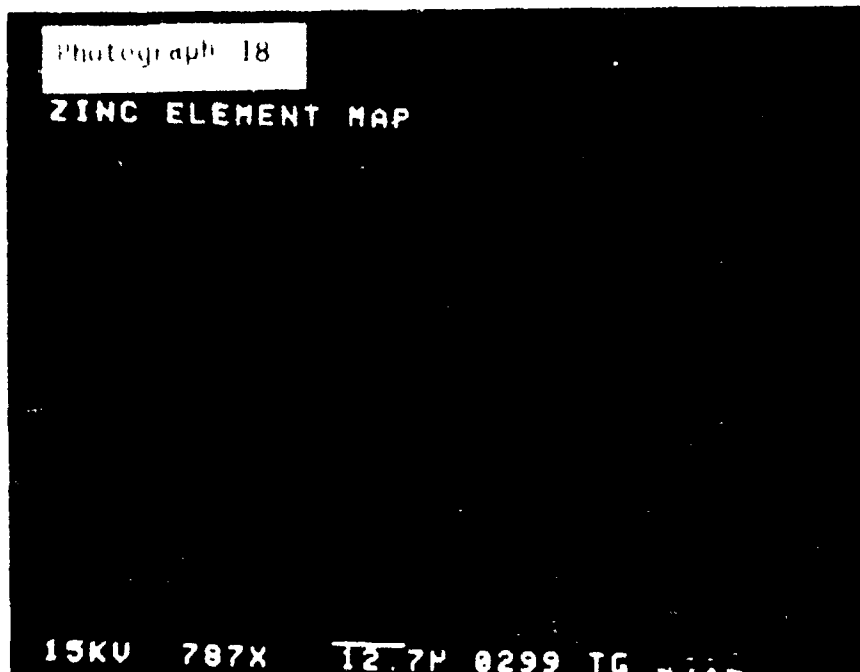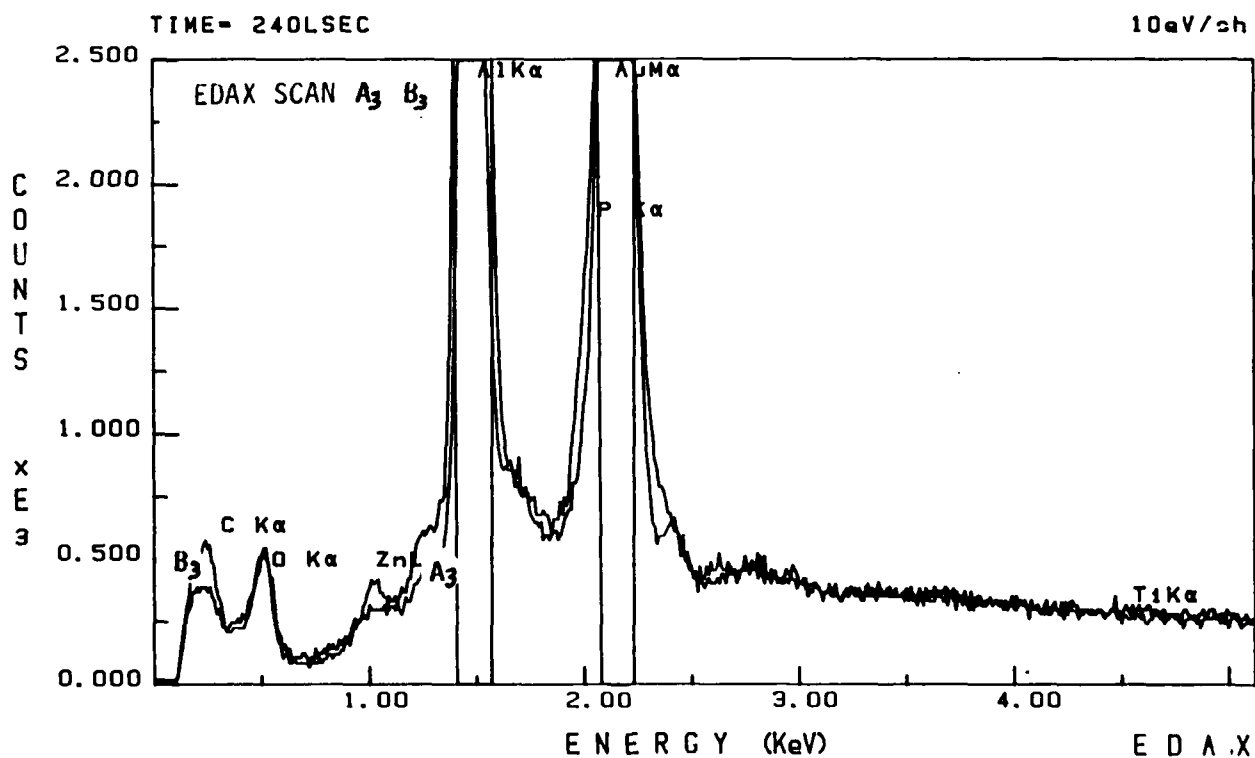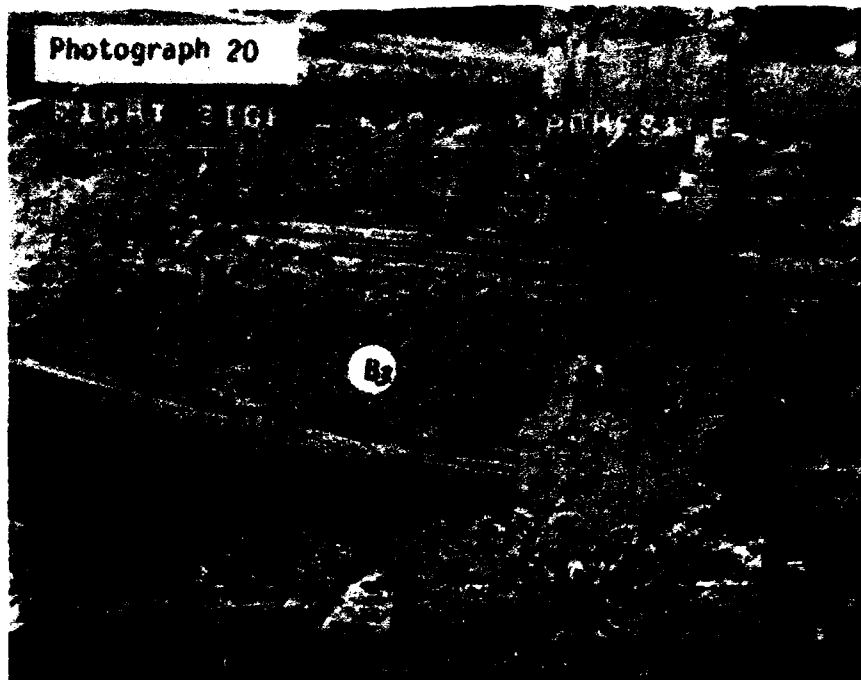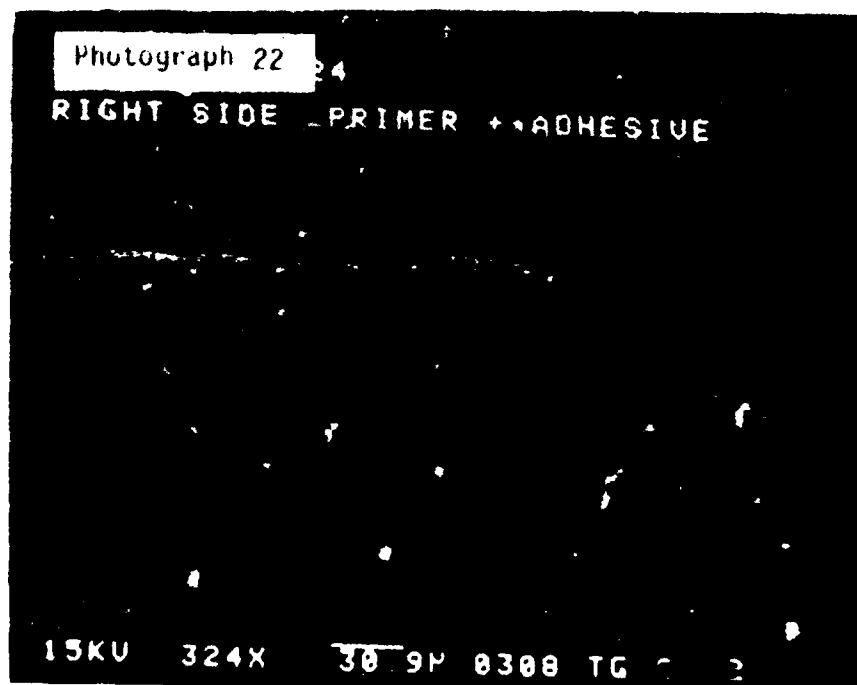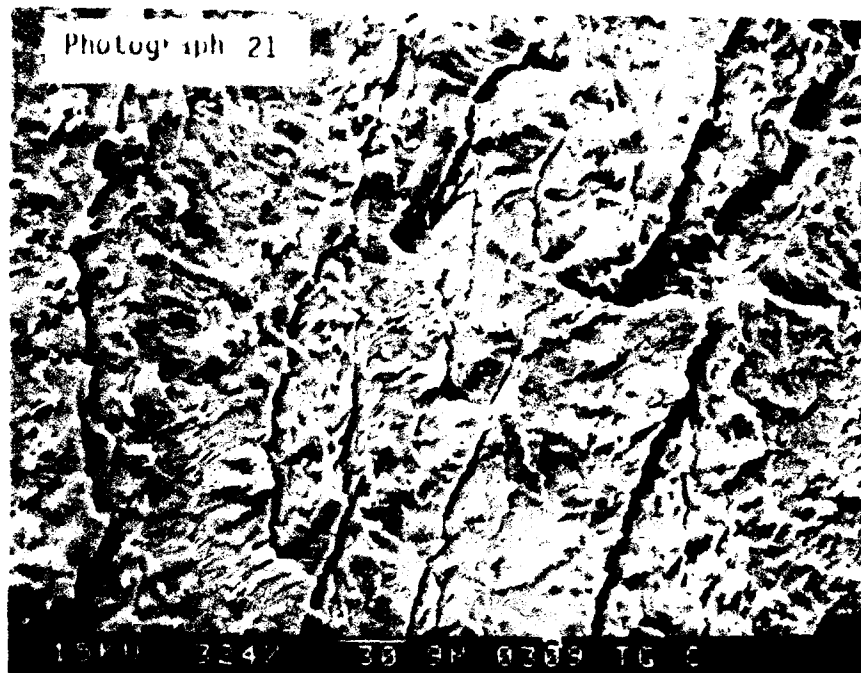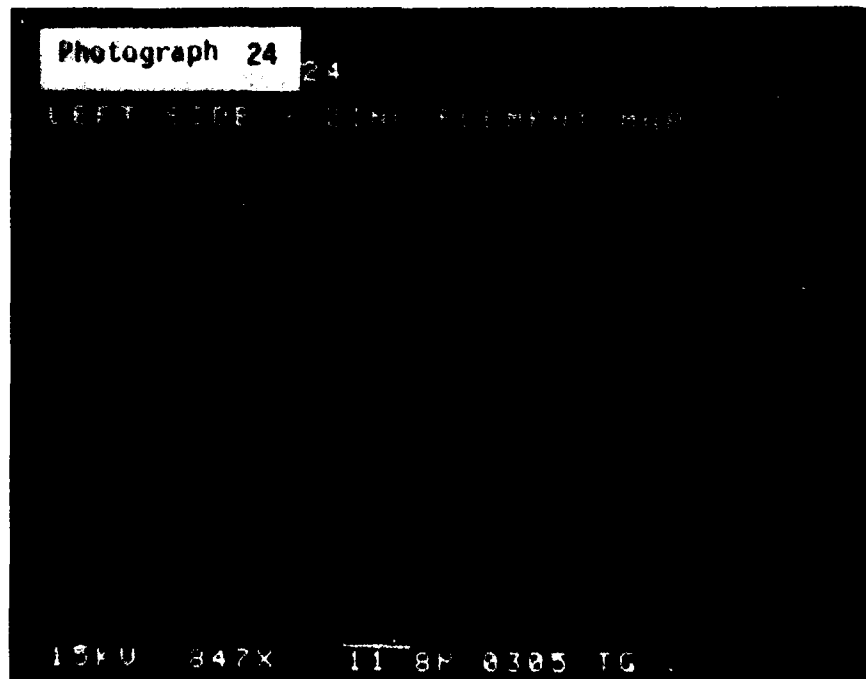
APPENDIX E

TRIAL ELECTRODEPOSITION PRIMING PROCEDURE, THIRD BATCH

MATERIALS:

- E.D. Primer, XA-3995 (Batch #3)
- D.I. water of pH 6.2-6.5
- Solvents:
    a. 2-butoxy ethanol or butyl cellusolve
    b. Methyl isobutyl ketone (MIBK)
    c. Xylenes
- 2024-T81 alloys

TASKS:

Perform the following tasks with 3M personnel.

A. Evaluate E.D. primer Batch #2 with 3M personnel as follows:

1. Anodize and inspect aluminum details per production, MPD 02057 (RPS 17.23) method.

    NOTE: 10 L/S panels are needed by 8 a.m. and the others by 2 p.m.

2. Electroprime surface-treated panels at 30 volts and 8 seconds using automatic time-control unit within 4 hours of surface treatment.

3. Record and maintain the temperature of primer bath at 70-72°F while performing this task.

4. Air-dry the electroprimed panels at room temperature (R.T.) for 20-30 minutes and cure the panels at 350°F for 60-70 minutes using circulating air oven.

5. Measure and record the primer thickness of the specimens.

TRIAL ELECTRODEPOSITION PRIMING PROCEDURE, THIRD BATCH

B. Prepare the primer bath (Batch #3) under the direction of the principal investigator and 3M personnel as follows:

PROCEDURE TO DILUTE E.D. PRIMER BATCH

1. Empty the contents of a 1-gallon can of XA-3995 concentrate into a clean, lined 5-gallon pail.

2. Equip the pail with a high-speed stirrer motor and a "Hi-lift" propeller stirrer blade.

3. Weigh out 1151.5 grams (25.5 lbs or 3 gallons) of distilled or well-deionized water. The pH of deionized water should be 6.3-6.5.

4. Stir the XA-3995 concentrate at high speed. Slowly add the DI water to the XA-3995 concentrate. The rate of addition should be such that the 3 gallons of water is added over a time period of no less than 30 minutes. Adding the water too rapidly or adding the concentrate to water could cause irreversible coagulation of the primer.

5. Transfer diluted primer to the 6-gallon electrocell.

6. Repeat the above steps (1 to 5) for another 1-gallon can of XA-3995 concentrate primer.

7. Diluting both gallons of concentrate primer should yield about 8 gallons of XA-3995 at 10-percent solids (level).

8. Cover the electrocell adequately to prevent solvent evaporation.

TRIAL ELECTRODEPOSITION PRIMING PROCEDURE, THIRD BATCH

9. The E.D. primer bath requires continuous agitation and the temperature control of 70 ±1°F. Therefore, control parameters by using specially-equipped pump and heat exchanger.

C. Perform chemical analysis as follows:

1. Perform solvent analysis (3M).

2. Determine the following properties of primer bath:

   - Resistance
   - pH
   - Percent of content

   NOTE: Analysis should be performed daily in periods of heavy usage of the primer bath. Perform analysis at the end of the day so that solvent addition can be made to allow time for the solvent to equilibrate with resin overnight.

D. Electroprime the surface-treated specimens as described in Task A.

   NOTE 1: Anodize 10 panels of 2024-T81 Al for Tuesday morning at 8 a.m. and 30 panels (of 2024-T81) for Tuesday afternoon at 1 p.m.

   2: Cure 5 panel sets by placing them in a preheated oven at 350°F and 5 panel sets placed in an R.T. oven and then raising the temperature to 350°F at 6-8°F/minute. Cure for 60-70 minutes at 350-360°F.

E. Store the specimens with proper identification. Submit the data and relevant information to the principal investigator.

APPENDIX F

ANALYSIS - ELECTRODEPOSITED PRIMED ADHERENDS

Photograph #1

Photograph #1 is a macrophotograph of a primed panel lap shear coupon. A very irregular deposition of the primer is apparent. The primer, which has not been cured, appears to vary significantly in thickness and uniformity as judged by the varying degrees of opacity shown. After cure (fusion), the primer becomes transparent and the maximum variation in thickness seldom exceeds 35 percent between the thinnest and thickest portions (center, edges) of the coupon. The non-uniform areas seen in the uncured coating do remain, but not to the extent one would imagine based on opacity. Measured thickness variation extremes are generally within 20 to 25 percent for any given area.

Photograph #2

Photograph #2 is a SEM photomicrograph taken at 428X of the surfaces of uncured primer. The craters seen are suspected to be due to hydrogen gas bubbles emanating from small 5-10 micron diameter holes reaching to the surface of the substrate. The angular shapes are corrosion resistant pigment particles. During cure (fusion), the holes close and the craters flatten with the leveling action (flow) of the primer (see Photograph #3).

Photograph #3

Photograph #3 is a SEM photomicrograph taken at 920X of the surface of cured XA-3995. The crater/hole topography of the uncured XA-3995 surface seen in Photograph #2 has completely disappeared. Only the corrosion resistant pigment particles remain as prominent topography.
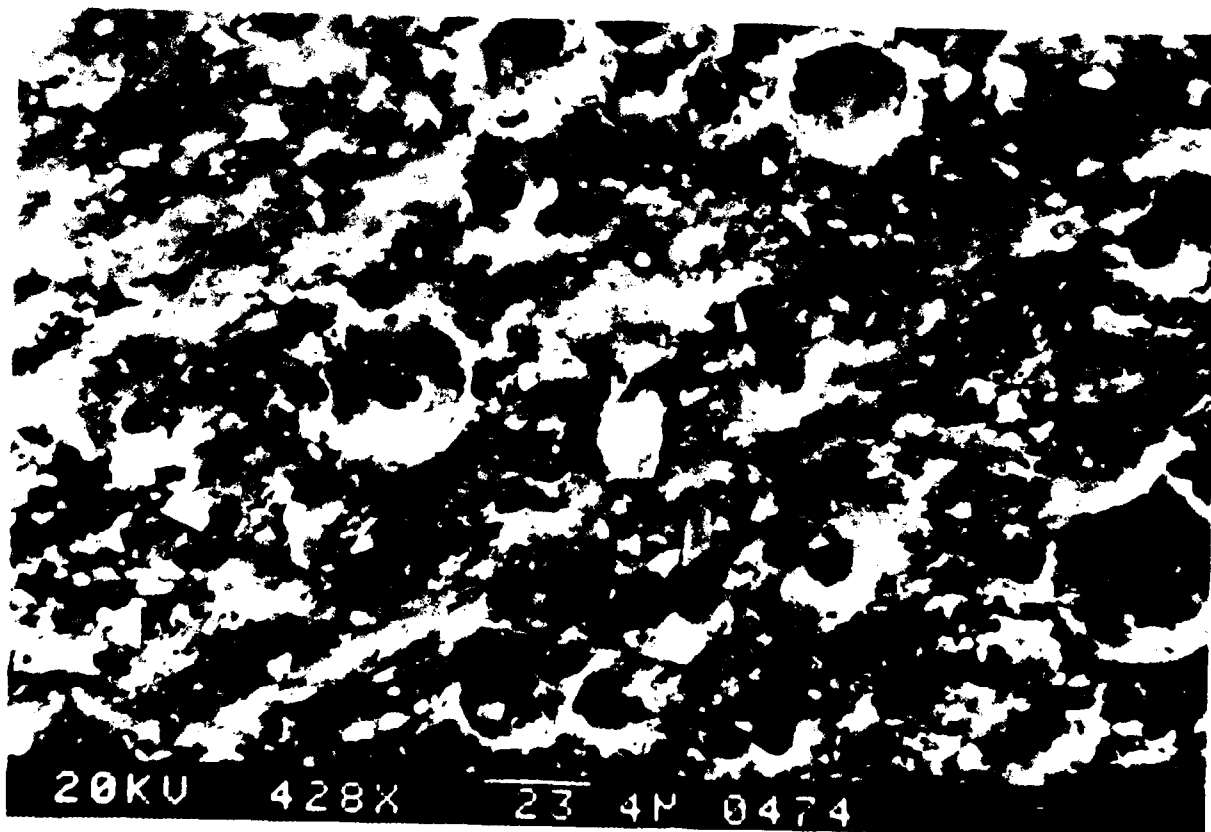
Photograph #4

Photograph #4 is a SEM X-ray map of Photograph #3 for the element aluminum. The opacity to X-ray is apparent in the areas covered by the corrosion resistant pigment particles. In the remaining area, the strong aluminum response is indicative of a thin organic coating as evidenced by the degree of penetration to the underlying aluminum surface.
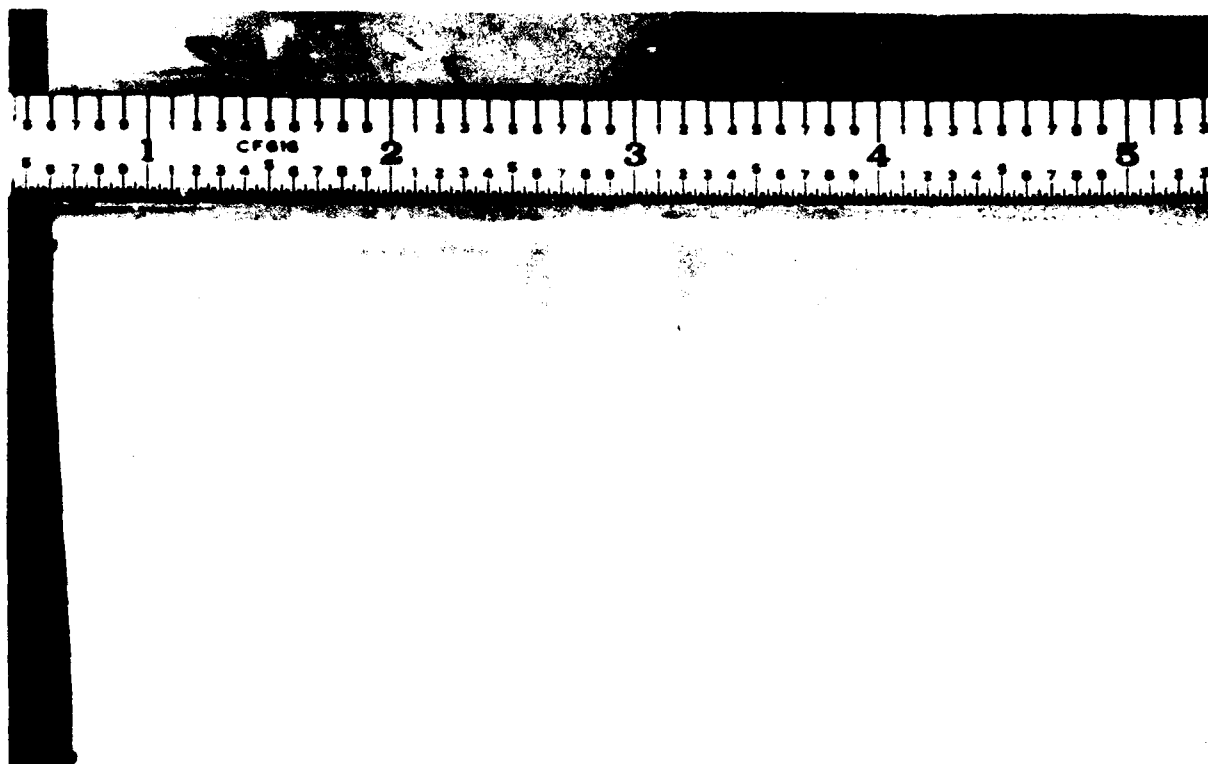
ANALYSIS - ELECTRODEPOSITED PRIMED ADHERENDS

PHOTOGRAPH #1

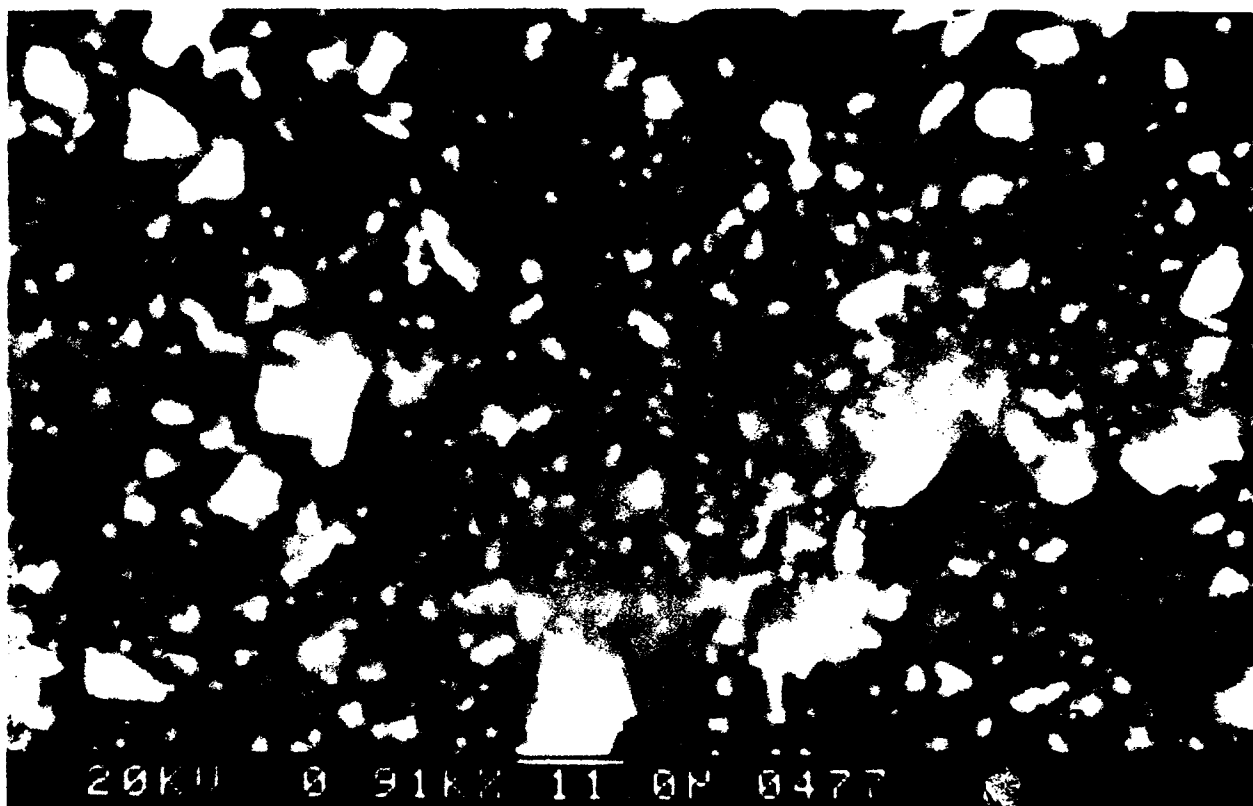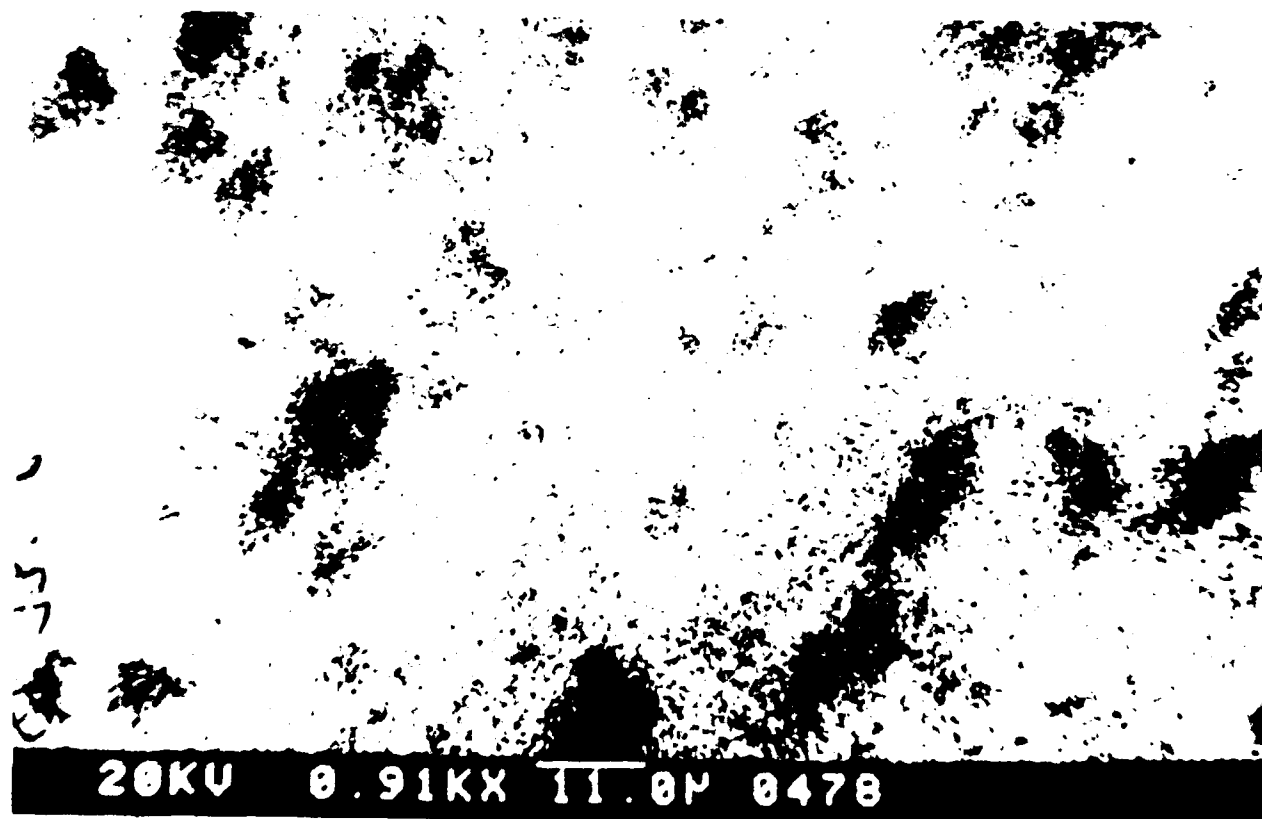

20KV   428X   23 4M 0474

PHOTOGRAPH #2

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PHOTOGRAPH #3

PHOTOGRAPH #4

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Photograph #5

Photograph #5 is an optical photomicrograph taken at 150X of a cured primed panel. This panel was one which failed a conductivity test for coating porosity. The primer coating is transparent in the cured state. Looking through the primer, the grain structure of the underlying aluminum substrates can be seen.

The areas ringed by the darker contrast (see arrows) are voids reaching to the metal surface. These areas are reflective by observation and emanate hydrogen gas/red discoloration under void detection (electrolysis) experiments. The size of these void areas range from 100 to 200 microns, approximately one magnitude greater in area than the porosity shown in Photograph #2. Although not apparent in Photograph #5, the void areas are miniature "fish-eyes" (exhibit surface tension effects). The "fish-eye" condition can be seen in Photograph #6.
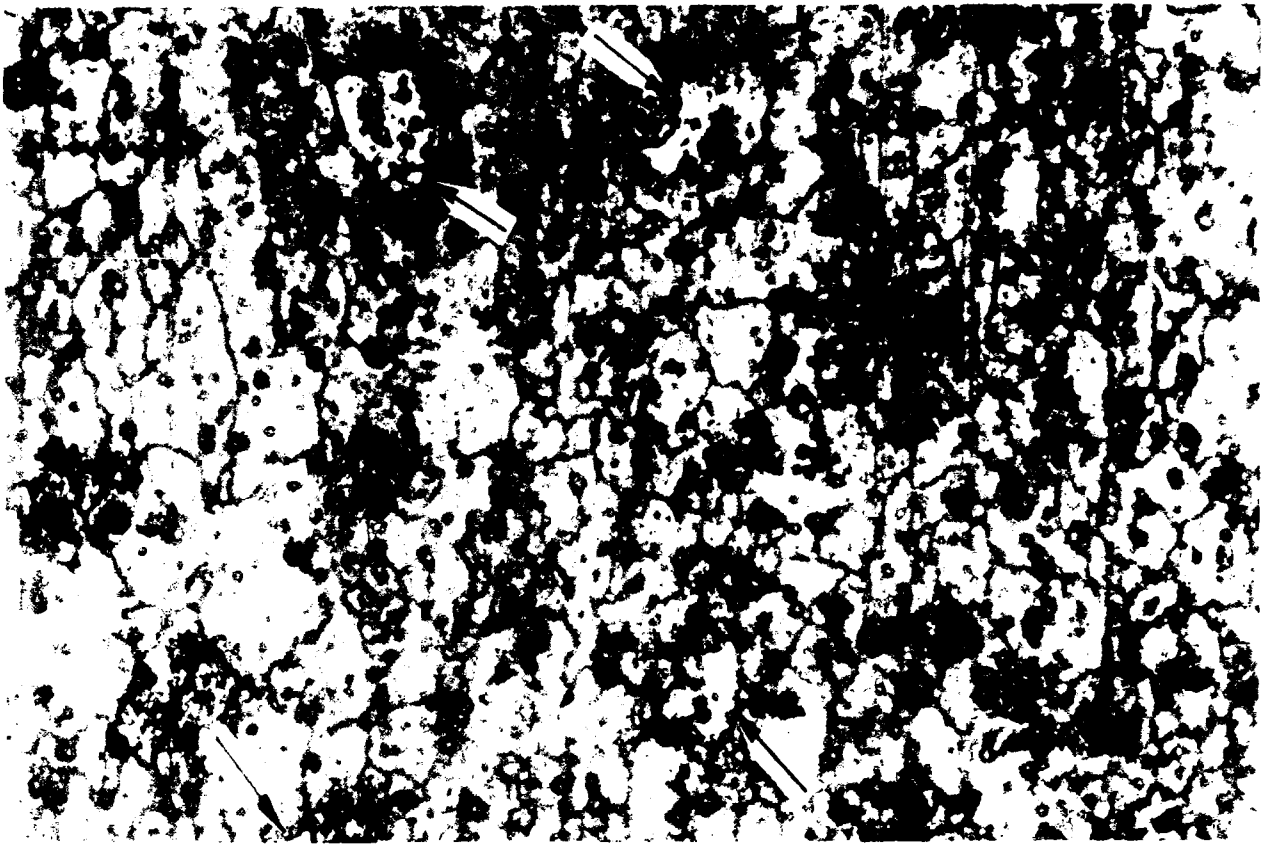
Photograph #6

Photograph #6 is an optical dark field photomicrograph taken at 450X of an area in a cured XA-3995 primed panel. This panel failed the leak detection test. Using dark field illumination, the cratered surface topography is more evident than with normal vertical illumination. The bottom surfaces of the craters are reflective (bare aluminum) and contain some debris in the form of resin and pigment particles.
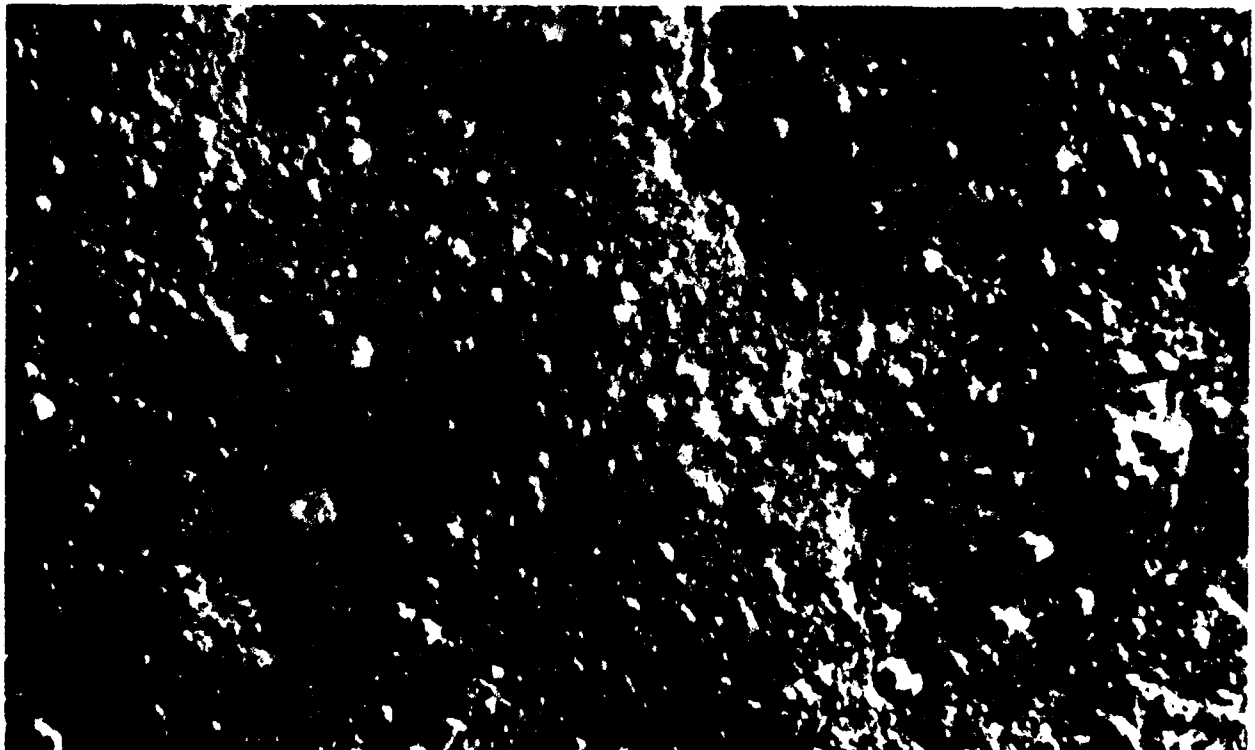
Photograph #7

Photograph #7 is a SEM photomicrograph taken at 17X of a cured primed panel. The darker portions of the photograph are thick primer areas which form ridges around the lighter (thinner) cratered portion of the surfaces. These craters are quite large, measuring 500 to 1000 microns across. Although the presence of bare metal cannot be determined for certain at the bottom of the craters, it is thought that a thin layer of primer completely covers the bottom areas. This coincides with optical microscopy observations which reveal an "orange-peel" surface without any "bare metal" reflection showing.

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PHOTOGRAPH #5

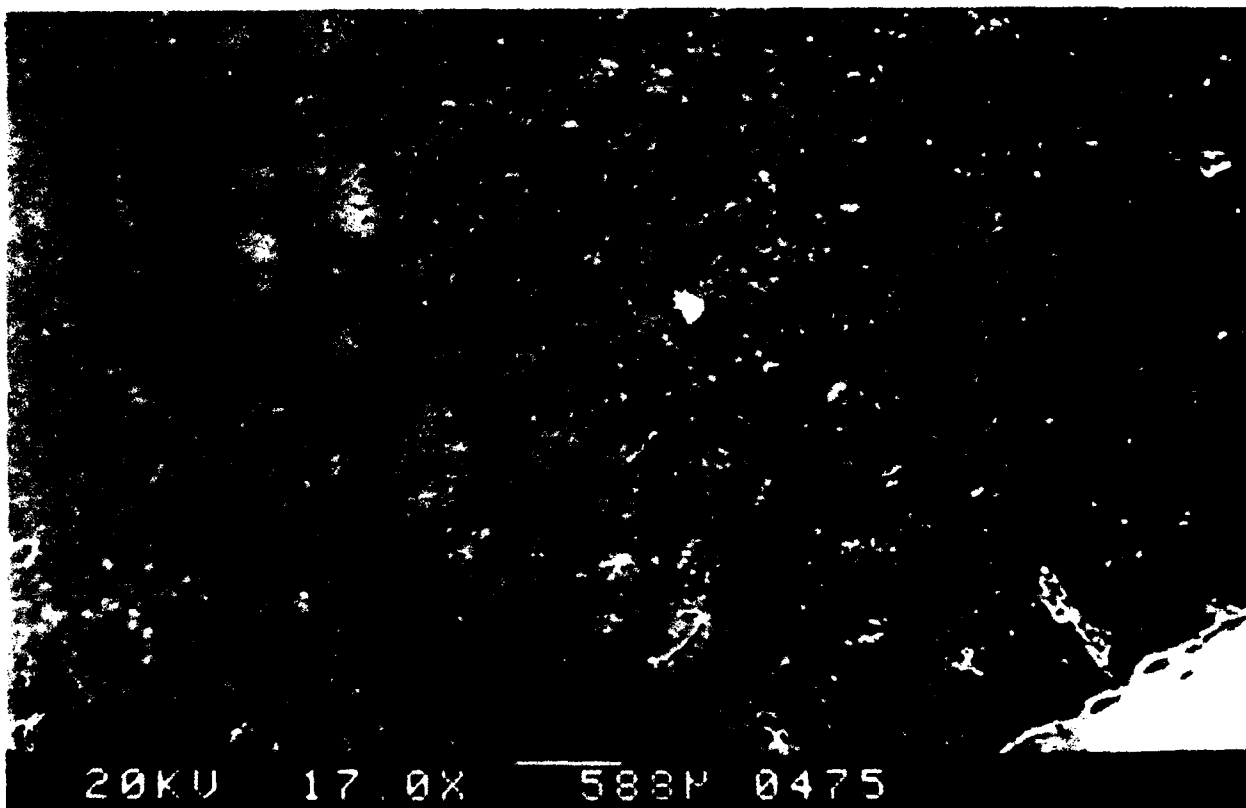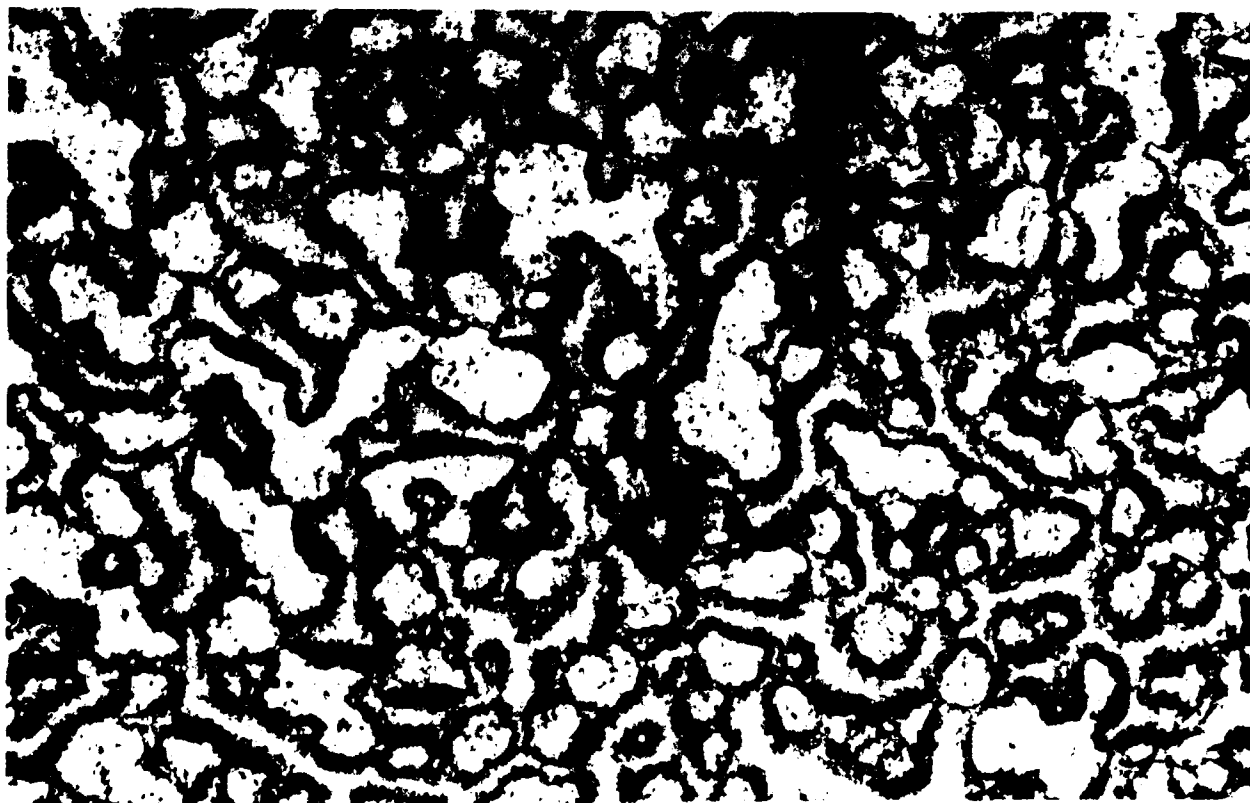

PHOTOGRAPH #6

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PHOTOGRAPH #7

PHOTOGRAPH #8

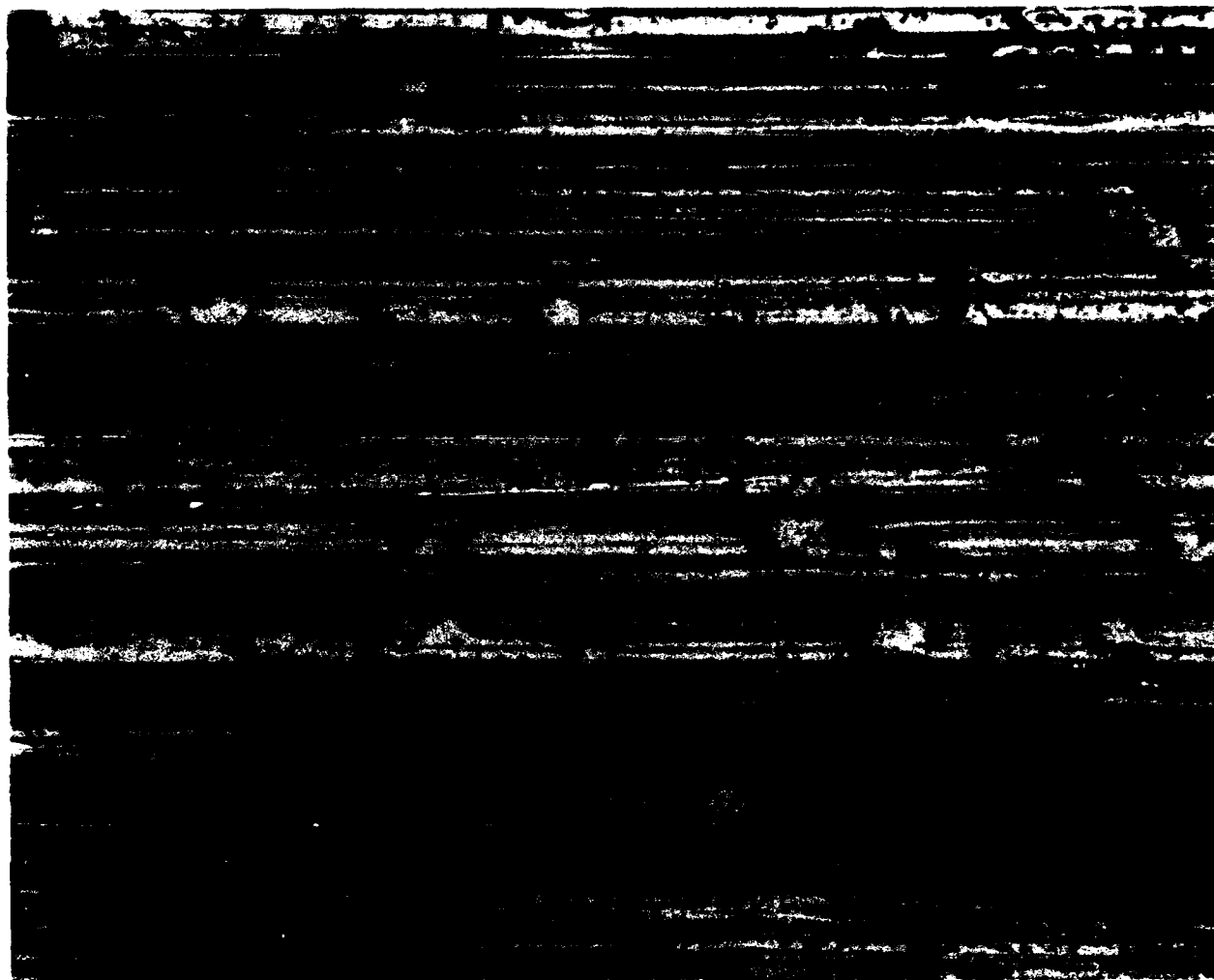## ANALYSIS - ELECTRODEPOSITED PRIMED ADHERENDS

Photograph #8

Photograph #8 is an optical photomicrograph taken at 150X of a cured primed panel. This panel demonstrates significant leakage in the conductivity test. The primer can be seen to have beaded/reticulated away from the surface of the specimen. A reflective metallic surface with localized resin and pigment debris is evident in the bottom portions of the craters/reticulations. This condition was seen in varying degrees in several panels, notably panels coated with primer which was more than 30 days old. The reticulated condition was not seen prior to primer cure but appears to have developed during the melt-and-flow period of the cure cycle.

Photograph #9

Photograph #9 is an optical photomicrograph taken at 150X of a cured primed panel of aluminum foil which has been FPL-cleaned but has not been phosphoric acid anodized. Observation of the panel prior to cure revealed an opaque coating of varying thickness similar to that seen in Photograph #1. The purpose of this experiment was to witness the reduced bond strength reported by 3M of the primer-to-aluminum surfaces which had not been phosphoric acid anodized. On flexing the primed foil adherend, the primer was observed to readily crack and to detach at moderate bend radii. Primed non-PAA treated specimens which had not been disturbed prior to cure (Photograph #9) were examined for leakage. The leakage test revealed significant porosity over the entire test coupon. Photograph #9 reveals numerous "fish-eye" type surface tension voids in the 100-micron size range.

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PHOTOGRAPH #9